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# Sur l'évaluation du nombre des paramètres éssentiels dont dépend la famille des intégrales d'un système d'équations différentielles ayant une propriété asymptotique

par

## T. WAŻEWSKI

La note présente donne une évaluation, par voie topologique, du nombre des paramètres essentiels dont dépend la famille des intégrales du titre. Pour la démonstration je tiens compte d'un lemme topologique sur la dimension (au sens de Menger-Urysohn) que j'ai formulé et qu'ont démontré K. Kuratowski et K. Borsuk; je tiens à leur adresser mes remerciements.

Le théorème 1 a été énoncé de façon à être relativement simple. Il est cependant doué de différents remaniements qui gardent les propriétés topologiques de ses hypothèses. Sa démonstration peut être ramenée au lemme ci-dessus à l'aide de notre théorème antérieur qui fournit une méthode topologique de l'examen du parcours asymptotique des intégrales des équations différentielles (cf. [1]).

I. Posons $X = (x_1, \ldots, x_p)$, $Y = (y_1, \ldots, y_q)$. Admettons que les deuxièmes membres du système de $p + q$ équations différentielles, écrit sous la forme vectorielle

$$(1) \qquad X' = f(t, X, Y), \quad Y' = g(t, X, Y),$$

soient continus dans un ensemble ouvert $W$ contenu entre les plans

$$t = a \quad \text{et} \quad t = b \quad (\text{où} -\infty \leqslant a < b \leqslant +\infty),$$

et que par chaque point $P \in W$ passe une seule intégrale $J(P)$ de (1) (prolongée à gauche et à droite jusqu'à la frontière de $\overline{W}$).

Désignons par $J_+(P)$ la partie de $J(P)$ qui contient le point $P$ et les points de $J(P)$ situés à droite de $P$.

II. Envisageons dans l'espace des points à $p + q + 1$ dimensions $(t, X\ Y)$ le tuyau $T \subset W$ défini par les relations

$$|X - L(t)| \leqslant l(t) > 0, \quad |Y - M(t)| \leqslant m(t) > 0, \quad t \, \epsilon \, D,$$

où $D$ désigne l'intervalle ouvert $a < t < b$.

Admettons que les fonctions vectorielles données $L$ et $M$, et les fonctions numériques $l$ et $m$, soient continuement dérivables dans $D$. $J_+(P)$ sera dite asymptotique relativement à $T$, $W$ et au système (1), lorsque $J_+(P) \subset T$. Elle sera alors définie pour $t_0 \leqslant t < b$, où $t_0$ est la première coordonnée de $P$.

III. Introduisons les sous-ensembles de $T$ définis par les relations

$$|X - L(t)| = l(t), \quad |Y - M(t)| \leqslant m(t), \quad t \, \epsilon \, D \quad \text{(face } \bar{E}\text{)},$$
$$|X - L(t)| \leqslant l(t), \quad |Y - M(t)| = m(t), \quad t \, \epsilon \, D \quad \text{(face } \bar{S}\text{)}.$$

Posons

$$G = \bar{E} \cdot \bar{F}, \quad E = \bar{E} - G, \quad F = \bar{F} - G,$$

et admettons les inégalités suivantes:

$$[X - L(t)] [f(t, X, Y) - L'(t)] < l'(t)\, l(t) \quad \text{pour} \quad (t, X, Y) \, \epsilon \, \bar{E},$$
$$[Y - M(t)] [g(t, X, Y) - M'(t)] > m'(t)\, m(t) \quad \text{pour} \quad (t, X, Y) \, \epsilon \, \bar{S}.$$

Ces inégalités expriment que:

1° l'intégrale $J(P)$ qui passe par $P \, \epsilon \, G$ glisse extérieurement sur $T$ en touchant la frontière latérale $\bar{E} + \bar{S}$ de $T$ au point isolé $P$,

2° $J(P)$ traverse la frontière latérale de $T$ en passant, pour $t$ croissant, de l'intérieur à l'extérieur de $T$ lorsque $P \, \epsilon \, S$ ($P$ est point de sortie au sens strict),

3° $J(P)$ traverse la frontière latérale dans le sens inverse lorsque $P \, \epsilon \, E$ ($P$ est point d'entrée au sens strict).

IV. Désignons par $T_0$ la section de l'ensemble $T$ par le plan $t = t_0$.

Théorème 1. *Admettons les hypothèses précédentes et envisageons la classe $Z$ des points $P \, \epsilon \, T_0$ tels que la demi-intégrale $J_+(P)$ soit asymptotique relativement à $T$, $W$ et au système (1).*

*Ceci posé le nombre de dimensions de $Z$ est $\geqslant p$. Autrement dit, le nombre des paramètres essentiels dont dépend la famille des intégrales asymptotiques relativement aux ensembles $W$ et $T$ et au système (1) est au moins égal à $p$.*

V. Voici l'esquisse de la démonstration.

Posons $\bar{S}_0 = \bar{S} T_0$, $\bar{E}_0 = \bar{E} T_0$. En se basant sur le théorème 1. mentionné ci-dessus, on peut démontrer que l'ensemble $Z$ a les propriétés suivantes:

Il est fermé et $Z \subset T_0 - \bar{S}_0$. Dans chaque ensemble $Q$ tel que $Q \subset T_0$, que $Q\bar{S}_0$ ne soit pas un rétracte de $Q$ mais que $Q\bar{S}_0$ soit un rétracte de $\bar{S}_0$, — il se trouve un point au moins qui appartient à $Z$.

Il en résulte — comme l'ont prouvé K. Kuratowski et K. Borsuk — que le nombre de dimensions de $Z$ est $\geqslant p$, c'est-à-dire que $dim(Z) \geqslant p$, ce qui termine la démonstration.

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# Sur une méthode · de comparaison des équations hyperboliques aux dérivées partielles du second ordre avec les équations différentielles ordinaires

par

## J. SZARSKI et T. WAŻEWSKI

*Présenté par T. WAŻEWSKI à la séance du 20 Octobre 1952*

Considérons l'inégalité différentielle aux dérivées partielles du second ordre de la forme

$$(1) \qquad \left| \sum_{i,k=1}^{m} a_{ik}(x_1, \ldots, x_m) \frac{\partial^2 u}{\partial x_i \partial x_k} \right| \leqslant \sum_{j=1}^{m} |b_j(x_1, \ldots, x_m)| \cdot \left| \frac{\partial u}{\partial x_j} \right| + $$
$$+ |c(x_1, \ldots, x_m)| \cdot |u| + |f(x_1, \ldots, x_m)|,$$

où l'opérateur différentiel

$$(2) \qquad H[u] = \sum_{i,k=1}^{m} a_{ik}(x_1, \ldots, x_m) \frac{\partial^2 u}{\partial x_i \partial x_k}$$

est du type hyperbolique normal. Il s'agit dans cette note d'évaluer l'intégrale

$$(3) \qquad U[u]_x = \int_{S_x} \int \left[ \sum_{i=1}^{m} \left( \frac{\partial u}{\partial x_i} \right)^2 + u^2 \right] dx_1 \ldots dx_{m-1},$$

où $u(x_1, \ldots, x_m)$ est une fonction de classe $C^2$ satisfaisant à l'inégalité (1) dans un domaine $\Omega$, et $S_x$ désigne l'intersection du domaine $\Omega$ par l'hyperplan $x_m = x$. La méthode consiste à trouver une inégalité différentielle ordinaire à laquelle satisfait la fonction

$$(4) \qquad E(x) = \int_{S_x} \int \left[ \sum_{i,k=1}^{m-1} a_{ik} \frac{\partial u}{\partial x_i} \frac{\partial u}{\partial x_k} - a_{mm} \left( \frac{\partial u}{\partial x_m} \right)^2 + u^2 \right] dx_1 \ldots dx_{m-1}.$$

L'intégration de cette inégalité fournit l'évaluation de $E(x)$ et par conséquent de $U[u]_x$, car dans les hypothèses du théorème qui suit, on a

$$(5) \qquad\qquad U[u]_x \leqslant \frac{1}{\nu}\,E(x),$$

où $\nu > 0$ est une constante convenable. Voici l'énoncé de notre théorème.

Théorème. Supposons que:

1º $a_{ik}(x_1, \ldots, x_m)$ sont de classe $C^1$,

2º $b_j(x_1, \ldots, x_m)$, $c(x_1, \ldots, x_m)$, $f(x_1, \ldots, x_m)$ sont continues,

3º $\sum\limits_{i,k=1}^{m-1} a_{ik}(x_1, \ldots, x_m)\lambda_i \lambda_k$ est une forme quadratique positive, définie,

4º $a_{mm}(x_1, \ldots, x_m) < 0$,

pour tout point $(x_1, \ldots, x_m) \epsilon \,\Omega$, où $\Omega$ est un domaine fermé et borné dont la frontière est composée des intersections $S_0$ et $S_{x_0}$ du domaine $\Omega$ par les hyperplans $x_m = 0$ et $x_m = x_0 > 0$, et d'une surface latérale de classe $C^1$, $L$ à $n-1$ dimensions qui est la somme de deux ensembles $L_E$ et $L_T$.

En désignant pour une fonction $G(x_1, \ldots, x_m)$ de classe $C^1$

$$A[G(x_1, \ldots, x_m)] = \sum_{i,k=1}^{m}{}' a_{ik}(x_1, \ldots, x_m)\frac{\partial G}{\partial x_i}\frac{\partial G}{\partial x_k},$$

convenons que la surface, donnée par l'équation $G = 0$, possède au point $(\overset{\circ}{x}_1, \ldots, \overset{\circ}{x}_m)$ l'orientation caractéristique, resp. celle dans l'espace, resp. celle dans le temps par rapport à l'opérateur (2), suivant que

$$A[G(\overset{\circ}{x}_1, \ldots, \overset{\circ}{x}_m)] = 0, \quad \text{resp.} \quad A[G(\overset{\circ}{x}_1, \ldots, \overset{\circ}{x}_m)] < 0, \quad \text{resp.} \quad A[G(\overset{\circ}{x}_1, \ldots, \overset{\circ}{x}_m)] > 0.$$

Ceci dit, nous supposons que l'ensemble $L_E$ soit la somme d'un nombre fini de surfaces possédant en chaque point l'orientation caractéristique ou bien celle d'espace, et que $L_T$ soit la somme d'un nombre fini de surfaces orientées dans le temps (d'après 4º la surface $S_0$ qui fait partie de l'hyperplan $x_m = 0$ possède l'orientation d'espace). Nous admettons que $\cos(n, x_m) < 0$ sur $L_E$ et $\cos(n, x_m) > 0$ sur $L_T$, où $n$ désigne la normale intérieure. On suppose enfin que l'intersection $S_x$ du domaine $\Omega$ par l'hyperplan $x_m = x$ varie avec $x$ de façon à garantir la continuité par rapport à $x$ de l'intégrale $\iint\limits_{S_x}\psi(x_1, \ldots, x_m)\,dx_1 \ldots dx_{m-1}$ pour toute fonction continue $\psi$, et que chaque surface contenue dans l'ensemble $L_T$ admette une représentation paramétrique de classe $C^1$, régulière de la forme

$$x_i = \varphi_i(t_1, \ldots, t_{m-1}), \quad (i = 1, \ldots, m-1), \quad x_m = t_{m-1},$$

où $t_1, \ldots, t_{m-1}$ sont des paramètres. Posons pour une fonction $u(x_1, \ldots, x_m)$ de classe $C^2$ dans $\Omega$

$$(6) \qquad F(x) = \int\limits_{L_{T^x}}\Big[\sum_{i,k=1}^{m-1}{}' a_{ik}\frac{\partial u}{\partial \eta_i}\frac{\partial u}{\partial \eta_k} + u^2\Big]\cos(n, x_m)\,ds,$$

$$(7) \qquad g(x) = F(x) + \int\int_{S_x} f^2 \, dx_1 \ldots dx_{m-1}.$$

Dans la formule (6) l'intégrale est étendue sur la somme de surfaces à $n-2$ dimensions $L_{Tx}$ qui forment l'intersection de l'ensemble $L_T$ par l'hyperplan $x_m = x$, et $(\eta_1, \ldots, \eta_{m-1})$ sont des coordonnées curvilignes convenablement choisies sur $L_T$.

Dans ces hypothèses, pour toute fonction $u(x_1, \ldots, x_m)$ de classe $C^2$ satisfaisant à l'inégalité différentielle (1) dans $\Omega$, on a pour $0 \leqslant x \leqslant x_0$

$$(8) \qquad\qquad E(x) \leqslant \sigma(x),$$

où $\sigma(x)$ est l'intégrale de l'équation différentielle ordinaire

$$(9) \qquad\qquad y' = k_0(x)y + g(x),$$

issue du point $x = 0$, $y = E(0)$, et $k_0(x)$ est une fonction positive continue qui ne dépend que du domaine $\Omega$ et des coefficients figurant dans l'inégalité (1). Dans les mêmes hypothèses on a l'inégalité (5) et par conséquent

$$U[u]_x \leqslant \frac{1}{\nu} \, \sigma(x),$$

où $\nu$ désigne la valeur minimum sur la sphère unitaire de la forme positive définie (selon 3° et 4°),

$$\Phi(\lambda_1, \ldots, \lambda_{m+1}) = \sum_{i,k=1}^{m-1} a_{ik}\lambda_i\lambda_k - a_{mm}\lambda_m^2 + \lambda_{m+1}^2.$$

L'idée directrice de la démonstration est la suivante: on évalue en appliquant un artifice dû (cf. [1]) à S. Zaremba [2] la différence $E(x+h) - E(x)$ pour $h > 0$ et l'on obtient l'inégalité suivante

$$(10) \quad E(x+h) - E(x) \leqslant k_h(x)\int\limits_x^{x+h} E(\tau) \, d\tau + \int\limits_x^{x+h} g(\tau) \, d\tau \quad \text{pour} \quad 0 \leqslant x < x_0.$$

En divisant (10) par $h$ et en faisant tendre $h$ vers zéro, on déduit l'inégalité différentielle ordinaire

$$(11) \qquad \overline{D}_+ E(x) \leqslant k_0(x) E(x) + g(x) \quad \text{pour} \quad 0 \leqslant x < x_0,$$

où $\overline{D}_+$ désigne le nombre dérivé supérieur à droite. Or, les fonctions $E(x)$, $g(x)$, $k_0(x)$ étant continues, l'inégalité (8) résulte de (11) (cf. [3]).

Remarque 1. Le second membre de l'inégalité (8) ayant la forme

$$\sigma(x) = \left[ E(0) + \int\limits_0^x g(\tau) \exp\left(-\int\limits_0^\tau k_0(\varrho) \, d\varrho\right) d\tau \right] \exp\left(\int\limits_0^x k_0(\tau) \, d\tau\right),$$

il est clair d'après la définition de $E(x)$ et la formule (6), qu'il ne dépend que du domaine $\Omega$, des coefficients figurant dans (1), des valeurs initiales de Cauchy de la fonction $u$, données sur $S_0$, et des valeurs de $u$, données sur $L_T$. L'évaluation (8) est valable aussi dans le cas où l'un des ensembles $L_E$ et $L_T$ est vide. Lorsque $L_T$ est vide, on doit poser $F(x) \equiv 0$.

Remarque 2. Notre théorème peut être appliqué aux problèmes suivants concernant l'équation hyperbolique non-linéaire de la forme

$$\sum_{i,k=1}^{m} a_{ik}(x_1, \ldots, x_m) \frac{\partial^2 u}{\partial x_i \partial x_k} = f\left(x_1, \ldots, x_m, u, \frac{\partial u}{\partial x_1}, \ldots, \frac{\partial u}{\partial x_m}\right),$$

dont le second membre $f(x_1, \ldots, x_m, u, p_1, \ldots, p_m)$ satisfait à la condition de Lipschitz par rapport aux variables $u, p_1, \ldots, p_m$:

a) l'unicité de la solution du problème de Cauchy et du problème mixte,

b) l'évaluation de l'influence du changement des valeurs initiales de Cauchy, des valeurs aux limites et du second membre $f$, sur la solution $u$, la distance des deux solutions $u_1$ et $u_2$ étant entendue au sens de la norme

$$\|u_1 - u_2\|_x = U[u_1 - u_2]_x$$

Remarque 3. Le procédé conduisant à l'inégalité de la forme (10), pour une solution de l'équation hyperbolique, linéaire, appliqué pour la première fois par S. Zaremba [2], fut repris plus tard par Rubinowicz [4] et généralisé ensuite par Friedrichs et Levy [5]. Or, ces derniers auteurs, en partant de l'inégalité [10] pour $x = 0$ et en l'intégrant par rapport à $h$ dans l'intervalle $[0, l]$, ont obtenu l'inégalité

$$\int_0^l E(h)\,dh \leqslant k_0\, l \int_0^l E(\tau)\,d\tau + l \cdot \int_0^l g(\tau)\,d\tau + l E(0),$$

où $k_0 = \max_{[0,l]} k_0(x)$, laquelle donne l'évaluation de $\int_0^l E(\tau)\,d\tau$ en admettant $l < \dfrac{1}{k_0}$, c'est-à-dire pour $l$ suffisamment petit. Cependant notre méthode nous fournit l'évaluation de $E(x)$ dans l'intervalle entier $0 \leqslant x \leqslant x_0$.

Une méthode analogue à la nôtre fut appliquée par S. Sobolev [6] pour l'équation de l'onde sphérique, le domaine $\Omega$ étant un cylindre de la forme: $(x_1, \ldots, x_m) \in S$; $0 \leqslant x \leqslant x_0$. L'inégalité différentielle pour $U[u]_x$ est obtenue par cet auteur, dans ce cas-là, tout simplement par la différentiation sous le signe d'intégrale. Ce procédé n'est pourtant pas applicable dans le cas général.

Remarquons enfin que nous n'avons admis aucune hypothèse garantissant l'existence de la dérivée de la fonction $E(x)$, en remplaçant la dérivée ordinaire par le nombre dérivé supérieur à droite. Or, ceci fut possible grâce aux travaux de T. Ważewski [3] sur les inégalités différentielles contenant les nombres dérivés supérieurs ou inférieurs.

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# Sur les mouvements asymptotiques d'un point matériel mobile dans le champ des forces repoussantes

par

## Z. MIKOŁAJSKA

*Présenté par T. WAŻEWSKI à la séance du 27 Novembre 1952*

Soit $X = (x_1, \ldots, x_n)$ un point (de masse égale p. ex. à l'unité) mobile dans un champ de forces donné sous la forme vectorielle

$$(1) \qquad F = F(t, X, Y),$$

où $Y$ désigne la vitesse du point et $t$ le temps. Le champ $F$ sera dit repoussant (au sens général) lorsqu'on aura partout

$$(2) \qquad XF \geqslant 0,$$

où $XF$ désigne le produit scalaire des vecteurs en question. En particulier, le champ

$$(3) \qquad F = k(t, X, Y) \cdot X$$

où $k$ est un scalaire non négatif) qui est repoussant au sens ordinaire, satisfait à (2). Plus particulièrement, le champ l i n é a i r e de la forme

$$(4) \qquad F = A(t)X$$

où $A(t)$ désigne une matrice aux éléments dépendant d'une façon continue de $t$, est repoussant lorsqu'on admet (2).

L'équation du mouvement du point matériel en question aura la forme

$$(5) \qquad \ddot{X} = F(t, X, \dot{X}).$$

H y p o t h è s e H. Le champ $F$ est continu et satisfait à une condition quelconque garantissant l'unicité des intégrales du système (5).

D é f i n i t i o n. Le mouvement $X = X(t)$ conforme à la loi du mouvement (5) sera dit asymptotique au sens de A. Wintner lorsque la distance de $X(t)$ à l'origine des coordonnées, c. à d. au centre du repoussement, décroît au sens large à partir d'un instant $t_0$.

A. Wintner [1] a prouvé que l'équation l i n é a i r e (4) admet, dans le cas (2), une famille de mouvements asymptotiques (au sens précédent) qui dépend de $n$ paramètres essentiels.

En appliquant une méthode topologique due à T. Ważewski, on peut étendre ce résultat au cas des équations n·o·n l i n é a i r e s. Voici notre théorème:

T h é o r è m e. Dans l'hypothèse $H$ et dans la condition (2) l'équation (5) admet une famille de mouvements asymptotiques (au sens de A. Wintner) qui dépend au moins de $n$ paramètres essentiels.

Voici l'idée de la démonstration. L'équation (5) peut être remplacée par le système

$$(6) \qquad \dot{X} = Y, \quad \dot{Y} = F(t, X, Y).$$

Soit $X = X(t)$, $Y = Y(t)$ une intégrale quelconque de (6). On aura $Y = Y(t) = \dot{X}(t)$.

Soit $r = r(t)$ le carré de la distance entre $X(t)$ et l'origine des coordonnées. On aura $r = X^2$, $\dot{r} = 2XY$,

$$(7) \qquad \ddot{r} = 2\frac{d}{dt}(XY) = 2(XF + Y^2) \geqslant 0.$$

Envisageons dans l'espace à $2n$ dimensions des points $(X, Y)$, le domaine $D$ défini par l'inégalité $XY \leqslant 0$. Pour l'instant où l'intégrale du système (6) passe par un point $(X, Y)$ du domaine $D$ on aura $\dot{r}(t) \leqslant 0$. Donc, si à partir d'un instant $t_0$, une intégrale de (6) parcourt constamment dans $D$, la distance entre $X(t)$ et l'origine des coordonnées décroîtra constamment, au sens large. Il suffit donc de prouver qu'il existe une famille d'intégrales dépendant au moins de $n$ paramètres essentiels qui, à partir d'un $t = t_0$, appartiennent constamment à $D$.

Envisageons le domaine auxiliaire $G(a, b)$ défini par la relation $a \leqslant XY \leqslant b$ où $a < 0 < b$. Au cas où $b > 0$, la frontière de $G(a, b)$ se compose de la surface $S$ définie par la relation $XY = a$ et de la surface $E$ définie par la relation $XY = b$. En vertu de (2), de (7) et du fait que, sur $E + S$, on a $Y \neq 0$, nous avons $\frac{d}{dt}(XY) > 0$ pour les $(X, Y)$ appartenant à $E + S$. Il en résulte que les intégrales sortent de $G(a, b)$ à l'instant où elles rencontrent $S$ et entrent à l'intérieur de $G(a, b)$ à l'instant où elles rencontrent $E$, lorsque $t$ croît. En appliquant un théorème de T. Ważewski [2], on en conclut qu'il existe une famille $U(a, b)$ d'intégrales dépendant au moins de $n$ paramètres qui, à partir d'un instant $t_0$, parcourent constamment dans $G(a, b)$. Le passage à la limite $b \to 0$ associé d'un raisonnement convenable permet de prouver que la même propriété subsiste au cas $b = 0$. Comme $G(a, 0)$ fait partie de $D$, on en conclut qu'il existe une famille d'intégrales dépendant au moins de $n$ paramètres qui, à partir d'un instant $t_0$, parcourent constamment dans $D$, ce qui termine la démonstration.

Remarque 1. Notre théorème peut être appliqué aux équations linéaires à perturbation non linéaire suffisamment petite. Comme sa démonstration n'exigeait pas de comparaison avec un système linéaire, il peut donc être appliqué à bien des cas beaucoup plus généraux.

Remarque 2. En admettant que $XF > 0$ lorsque $X \neq 0$, on peut démontrer facilement que chaque intégrale asymptotique (au sens de Wintner) s'approche de l'origine des coordonnées au sens strict.

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# Angular Correlations of Three Successive Gamma Quanta

by

## J. DĄBROWSKI

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I. T h e o r y. Let us consider the following process: A nucleus in the initial excited state $j_1$ goes over to the first intermediate excited state $j_2$ by emitting a gamma quantum $(\vec{k}_1, 2^{L_1})$. The nucleus in the state $j_2$ then goes over to the second intermediate excited state $j_3$ by emitting a gamma quantum $(\vec{k}_2, 2^{L_2})$. Finally the nucleus in the state $j_3$ goes over to the ground state $j_4$ by emitting a gamma quantum $(\vec{k}_3, 2^{L_3})$. The $j$'s are the quantum numbers of the total angular momentum of the four states, while $(\vec{k}, 2^L)$ are the wave vector and multipolarity of the successive gamma quanta.

The probability of this process is given by the formula:

$$(1) \quad w = \sum \{m_1, m_4 M_1 M_2 M_3\} \Big| \sum \{m_2 m_3\} (j_1 m_1 | H(\vec{k}_1, M_1) | j_2 m_2)(j_2 m_2 | H(\vec{k}_2 M_2) | j_3 m_3) \cdot \\ \cdot (j_3 m_3 | H(\vec{k}_3 M_3) | j_4 m_4)|^2,$$

where $H(\vec{k}, M)$ is the interaction hamiltonian for emission of a gamma quantum with the wave vector $\vec{k}$. $M = \pm 1$ corresponds to the left- or right-handed circularly polarized wave respectively.

This formula can be derived by solving the perturbation theory equations by the Weisskopf-Wigner method. It is assumed that the nuclear states, which differ only with respect to the magnetic quantum numbers $m_r (r = 1, 2, 3, 4)$, have the same energy, and that the initial nucleus is oriented at random.

In Eq. (1), and also below, we omit constant factors, which are unimportant for the correlation formulae.

The matrix elements of the interaction hamiltonian $H(\vec{k}_s, M_s)(s = 1, 2, 3)$ for emission of a gamma quantum with the wave vector

$$(2) \qquad \vec{k}_s = k_s(\vec{i}_x \cos \varphi_s \sin \vartheta_s + \vec{i}_y \sin \varphi_s \sin \vartheta_s + \vec{i}_z \cos \vartheta_s)$$

and multipolarity $2^{L_s}$ have the form (Goertzel 1946):

$$(3) \qquad (j_s m_s \,|\, H(\vec{k}_s M_s) \,|\, j_{s+1} m_{s+1}) =$$

$$= \text{const} \sum_{\mu|-L_s}^{L_s} D^{(L_s)}(\varphi_s \vartheta_s 0)_{\mu} \,_s M_s^{\varepsilon}(j_{s+1} L_s j_s m_s \,|\, j_{s+1} L_s m_{s+1} \mu),$$

where $\varepsilon = 0,1$ for magnetic and electric transitions respectively, and the "const" is independent of $m_s$, $m_{s+1} M_s \cdot D^{(L_s)}(\varphi_s \vartheta_s 0)_{\mu M_s}$ are matrices of the irreducible representation of the three-dimensional rotation group, and $j_{s+1} L_s j_s m_s \,|\, j_{s+1} L_s m_{s+1} \mu)$ are the Clebsch-Gordan coefficients (Wigner 1931).

The value of $w$ is independent of the direction which we choose for the axis of quantization, hence we take the "$z$" axis along the direction of propagation of the second quantum. This choice of the "$z$" axis enables us to perform the greatest possible number of summations, as Racah (1951) does for double correlations.

The result of this calculation is

$$(4) \quad w = \sum \{\mu \nu \lambda \geqslant 0\} R_{\mu\nu\lambda}(j_1 j_2 j_3 j_4 \,|\, L_1 L_2 L_3) P_{2\mu,\lambda}(\cos \vartheta_1) P_{2\nu,\lambda}(\cos \vartheta_3) \cos \lambda \varphi$$

where

$$(5) \quad \begin{cases} R_{\mu\nu\lambda}(j_1 j_2 j_3 j_4 \,|\, L_1 L_2 L_3) = r_{\mu\nu}(j_1 j_2 j_3 j_4 \,|\, L_1 L_3) A_{\mu\nu\lambda}(j_2 j_3 \,|\, L_2), \\ r_{\mu\nu}(j_1 j_2 j_3 j_4 | L_1 L_3) = W(j_2 j_2 L_1 L_1 | 2\mu j_1) W(j_3 j_3 L_3 L_3 | 2\nu j_4)(L_1 L_1 1 {-} 1 | L_1 L_1 2\mu 0) \cdot \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \cdot (L_3 L_3 1 {-}1 \,|\, L_3 L_3 2\nu 0), \\ A_{\mu\nu\lambda}(j_2 j_3 \,|\, L_2) = \sum \{m_3 M_2\}(j_3 2\nu m_3 + \lambda, -\lambda \,|\, j_3 2\nu j_3 m_3)\,(j_2 2\mu m_3 + M_2 + \\ \qquad + \lambda, -\lambda \,|\, j_2 2\mu j_2 m_3 + M_2) \cdot (j_3 L_2 m_3 M_2 \,|\, j_3 L_2 j_2 m_3 + M_2)(j_3 L_2 m_3 + \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad + \lambda M_2 \,|\, j_3 L_2 j_2 m_3 + M_2 + \lambda), \end{cases}$$

$W$ are the Racah (1942) coefficients (tabulated by Biedenharn 1952). $P_{n,\lambda}$ are the associated Legendre polynomials with Condon and Shortley's (1951) choice of phases $\varphi = \varphi_1 - \varphi_3$.

II. D i s c u s s i o n. We shall now discuss the limitation imposed on anisotropy. Owing to the properties of the Racah coefficients $W$ we have

$$(6) \qquad \mu \leqslant \min(L_1 j_2); \quad \nu \leqslant \min(L_3 j_3),$$

where e. g. $\min(L_1, j_2)$ is the lesser of the two numbers $L_1, j_2$. Moreover, thanks to the properties of the associated Legendre polynomials, we have

$$(7) \qquad \lambda \leqslant \min(2\mu, 2\nu).$$

The numerical values of the correlation coefficients for three dipole transitions are tabulated below. The values of the Clebsch-Gordan coefficients used here have been given by Condon and Shortley (1951). The rations of the Racah coefficients occurring in the expressions for $r'$ are taken from Arfken, Biedenharn and Rose (1952).

Table of the correlation coefficients for three dipole
transitions

$$r'_{\mu\nu} A'_{\mu\nu\lambda} = R'_{\mu\nu\lambda} = R_{\mu\nu\lambda}/R_{000}; \quad r'_{\mu\nu} = r_{\mu\nu}/r_{00}; \quad A'_{\mu\nu\lambda} = A_{\mu\nu\lambda}/A_{000}$$

$$R'_{100}$$

$$r'_{10}(j_2 j_2 j_3 j_4 \mid 11) = -\left|\sqrt{\frac{(2j_2-1)(2j_2+3)}{20 j_2(j_2+1)}}\right|$$

$$r'_{10}(j_2-1 j_2 j_3 j_4 \mid 11) = \left|\sqrt{\frac{(j_2+1)(2j_2+3)}{20 j_2(2j_2-1)}}\right\} \text{ independent of } j_3, j_4$$

$$r'_{10}(j_2+1 j_2 j_3 j_4 \mid 11) = \left|\sqrt{\frac{j_2(2j_2-1)}{20(j_2+1)(2j_2+3)}}\right|$$

$$A'_{100}(j_3 j_3 \mid 1) = \frac{3-4j_3(j_3+1)}{10\sqrt{(2j_3-1)j_3(j_3+1)(2j_3+3)}}$$

$$A'_{100}(j_3+1 j_3 \mid 1) = \frac{2j_3^2+9j_3+10}{10\sqrt{(2j_3+1)(j_3+1)(j_3+2)(2j_3+5)}}$$

$$R'_{010}$$

$$r'_{01}(j_1 j_2 j_3 j_4 \mid 11) = r'_{10}(j_4 j_3 j_1 j_2 \mid 11) \qquad \text{independent of } j_1, j_2$$

$$A'_{010}(j_3 j_3 \mid 1) = A'_{100}(j_3 j_3 \mid 1)$$

$$A'_{010}(j_3+1 j_3 \mid 1) = \frac{j_3[3-14j_3(j_3+1)]}{10(2j_3+3)\sqrt{(2j_3-1)j_3(j_3+1)(2j_3+3)}}$$

$$R'_{11\lambda}$$

$$r'_{11}(j_1 j_2 j_3 j_4 \mid 11) = r'_{10}(j_1 j_2 \quad \mid 11) r'_{01}(\quad j_3 j_4 \mid 11)$$

$$A'_{110}(j_3 j_3 \mid 1) = \frac{20j_3^4+40j_3^3-91j_3^2-111j_3+72}{35 j_3(j_3+1)(2j_3-1)(2j_3+3)}$$

$$A'_{110}(j_3+1 j_3 \mid 1) = \frac{(2j_3+3)j_3(64j_3^4+352j_3^3-979j_3-240)}{35(j_3+1)\sqrt{(2j_3-1)(2j_3+1)(2j_3+3)(2j_3+5)j_3(j_3+2)}}$$

$$A'_{111}(j_3 j_3 \mid 1) = \frac{3(-24j_3^4+148j_3^3+14j_3^2-165j_3+265)}{140(2j_3-1)j_3(j_3+1)(2j_3+3)}$$

$$A'_{111}(j_3+1 j_3 \mid 1) = \frac{3j_3(8j_3^4+44j_3^3+175j_3^2+274j_3-93)}{14(2j_3+3)(j_3+1)\sqrt{(2j_3-1)(2j_3+1)(2j_3+3)(2j_3+5)j_3(j_3+2)}}$$

$$A'_{112}(j_3 j_3 \mid 1) = \frac{9(8j_3^4+16j_3^3-84j_3^2-92j_3-15)}{70(2j_3-1)(j_3+1)j_3(2j_3+3)}$$

$$A'_{112}(j_3+1 j_3 \mid 1) = \frac{6j_3(8j_3^4+44j_3^3+70j_3^2+13j_3-30)}{35(j_3+1)(2j_3+3)\sqrt{(2j_3-1)(2j_3+1)(2j_3+3)(2j_3+5)j_3(j_3+2)}}$$

In the correlation formula (4) we assume that the counters distinguish the three quanta emitted in succession (energy differences or delayed coincidences). If it is impossible to distinguish the three quanta, one must put the counters in such a position that the angles between every two of these positions are equal.

Since the correlation formula (4) is sensitive to the sequence of the successive emitted quanta, observation of the triple gamma correlation can give us information about the location of the nuclear levels.

During my work on the triple correlation problem, there appeared a paper on the same problem by Arfken, Biedenharn and Rose (1951), followed by still another paper by the same authors (1952). The three authors perform the whole calculation for the special cases in which two of the radiations are parallel or antiparallel. In addition they consider the case of two radiations in a triple cascade with one radiation unobserved. Such experiments are significant only when one of the three quanta is difficult to observe, e. g. on account of small energy. Of course the most information and the clearest results are yielded by those experiments in which one is not limited to special positions of the counters. Hence I undertook the laborious task of calculating the correlation formulae for triple gamma radiation for arbitrary directions of emission.

The distinction between emission and absorption is irrelevant in the correlation formulae. So the theory presented above also describes the case of absorption followed by the emission of two cascade radiations.

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# On the Use of an Approximation Method in Dirac's Electrodynamics

by

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In his first paper concerning the new electrodynamics, Dirac deduced the Hamilton-Jacobi equations of motion. Later, Dirac [2] generalised his field equations in order to ensure a proper description of motion.

I believe that the relationship between Dirac's field equations and the equations of motion needs some further elucidation, as does the physical content of Dirac's theory. As Dirac's equations are non-linear, it is not easy to understand the conclusions that can be drawn from them.

To throw some light upon these matters one needs a technique to deal with these equations. I believe that in the important case of the motion of particles, the "new approximation method" provides us with the proper technique. This method was successfully applied in the case of the motion of bodies in a gravitational field [3], in the case of motion in an electromagnetic field [4] and recently even in the theory of motion in nuclear fields [5]. Here we shall show how this method can be applied to Dirac's new electrodynamics. It seems to me certainly superior to that indicated by Dirac and recently worked out by Cini [6].

Let us recall briefly the essential assumptions of the new approximation method.

We have a function $\varphi$ (it could just as well be a vector or tensor) characterising the field. We develop $\varphi$ with respect to an arbitrary small parameter $\varepsilon$; in practice the role of $\varepsilon$ is played by $c^{-1}$ ($c =$ velocity of light). We write:

$$(1) \qquad \varphi = \varphi + \varepsilon \varphi_1 + \varepsilon^2 \varphi_2 + \ldots = \sum_{l=0}^{\infty} \varepsilon^l \varphi_l.$$

The $l$ in $\varphi_l$ shows that $\varphi_l$ belongs to $\varepsilon^l$, or that $\varepsilon^l \varphi_l = \psi_l$ is of the $l-th$

order. Thus, absorbing the $\varepsilon$'s, we can write

$$(2) \qquad \varphi = \sum_{l=0}^{\infty} \underset{l}{\psi}.$$

Let us denote by Greek letters those indices that run from 0 to 3, and by Latin letters those that run from 1 to 3. Taking $c = 1$, we have $x^0 = ct = t$. Then the essential assumption is: the space derivatives of a function are of the same order as the function itself. But taking the derivative with respect to time raises the order of the function by 1. Thus:

$$(3) \qquad \underset{l}{\psi}_{,k} = \partial \underset{l}{\psi} / \partial x^k; \quad \text{but} \quad \underset{l}{\psi}_{,0} = \partial \underset{l}{\psi} / \partial x^0 = \underset{l+1}{\psi}_{,0}.$$

Our next step is to recall Dirac's theory of electrodynamics. The fundamental quantity in it is the vector potential $A_\alpha$. We define:

$$(4) \qquad f_{\alpha\beta} = A_{\beta,\alpha} - A_{\alpha,\beta}$$

and then Dirac's field equations are:

$$(5) \qquad f^{\alpha\beta}{}_{,\beta} = \lambda A^\alpha$$

$$(6) \qquad A^\alpha A_\alpha = k^2 = \left(\frac{mc^2}{e}\right)^2 = \left(\frac{m}{e}\right)^2, \quad \text{if} \quad c = 1.$$

These are five equations to determine the $A_\alpha$'s and $\lambda$. (We may mention that the quadratic form used here is $ds^2 = \eta_{\alpha\beta}\, dx^\alpha\, dx^\beta$, where $\eta_{ks} = -\delta_{ks}$, $\eta_{0s} = 0$, $\eta_{00} = 1$).

Now, in order to use the approximation method we have to develop $A_\alpha$. Thus $eA_0$ has the dimension of energy, $eA_k$ that of linear momentum. According to Dirac's theory $eA_0$ is the energy and $eA_k$ is the linear momentum of an electron. Therefore we shall develop $A_0$ and $A_k$ as we would have developed $m_0/\sqrt{1-v^2}$ and $m_0\vec{v}/\sqrt{1-v^2}$ with respect to $v$. Thus:

$$(7\,\text{a}) \qquad A_0 = \underset{0}{A_0} + \underset{2}{A_0} + \underset{4}{A_0} + \cdots$$

$$(7\,\text{b}) \qquad A_k = \underset{1}{A_k} + \underset{3}{A_k} + \underset{5}{A_k} + \cdots$$

Therefore in the normalisation condition $k^2$ is also of the order zero if $A_0$ begins with $\underset{0}{A_0}$.

Now there is no difficulty in defining the order of $f_{\alpha\beta}$. We have:

$$(8\,\text{a}) \qquad \underset{2l}{f_{0m}} = \underset{2l-1}{A_{m,0}} - \underset{2l}{A_{0,m}},$$

$$(8\,\text{b}) \qquad \underset{2l+1}{f_{mn}} = \underset{2l+1}{A_{n,m}} - \underset{2l+1}{A_{m,n}}.$$

Let us now develop the normalisation condition. We have

$$\underset{0}{A_0^2} = k^2$$

$$(9) \qquad 2\,\underset{0}{A_0}\underset{2}{A_0} - \underset{1}{A_k}\underset{1}{A_k} = 0 \quad \text{etc.}$$

Thus $\underset{0}{A_0} = \pm k$. The first expression in the development (7a) must be a constant. Therefore the field must start with the order o n e ($f_{mn}$ with the order o n e and $f_{0m}$ with the order t w o). This initial field, that is $\underset{1}{f_{mn}}$ and $\underset{2}{f_{0n}}$, is the given field in which the electron beam moves and by the motion of which it is modified. Therefore $\underset{1}{f_{mn}}$ and $\underset{2}{f_{0n}}$ are given by the nature of the particular problem. These initial $f's$ must satisfy Maxwell's equations for a vacuum under given boundary conditions.

The remaining question is that of the development of $\lambda$. The answer is:

$$(10) \qquad \lambda = \underset{4}{\lambda} + \underset{6}{\lambda} + \dots$$

Indeed, multiplying (5) by $A_\alpha$ we have:

$$(11) \qquad k^2 \lambda = A_\alpha f^{\alpha\varrho}{}_{,\varrho} = \underset{0}{A_0} f^{0\varrho}{}_{,\varrho} + \underset{1}{A_k} f^{k\varrho}{}_{,\varrho} + \dots$$

Since the initial $f's$ satisfy Maxwell's equations for a vacuum, the first expressions in (11) different from zero are

$$\underset{0}{A_0}\,\underset{4}{f^{0m}}{}_{,m} + \underset{1}{A_k}\,\underset{3}{f^{kn}}{}_{,n}.$$

Therefore $\lambda$ starts with $\underset{4}{\lambda}$ and the remaining expressions are of an even order.

We see that the only assumptions for the use of the "new approximation method" lie in (7) and in the assumption that the $f's$ of the lowest order satisfy Maxwell's equations for a vacuum.

We shall now distinguish between $A_\alpha$ and $A_\alpha^*$. The vector $A_\alpha$ is the solution of Dirac's equations (4—6). That is, $A_\alpha$ is properly normalised. The vector $A_\alpha^*$ may differ from $A_\alpha$ only by a gradient of an arbitrary function.

Now let us assume that we know:

$$(12) \qquad \underset{0}{A_0},\dots\underset{2l}{A_0}, \quad \underset{1}{A_k},\dots\underset{2l-1}{A_k}, \quad \underset{4}{\lambda},\dots\underset{2l}{\lambda}.$$

We shall write down the equations needed for the next approximation,

$$(13) \qquad (\underset{2l+2}{\lambda}\,\underset{0}{A_0} + \dots \underset{4}{\lambda}\,\underset{2l-2}{A_0})_{,0} - (\underset{2l+2}{\lambda}\,\underset{1}{A_k} + \dots \underset{4}{\lambda}\,\underset{2l-1}{A_k})_{,k} = 0,$$

$$(14) \qquad \underset{2l+1}{A_k^*}{}_{,ss} - \underset{2l+1}{A_s^*}{}_{,sk} = \underset{-2l-3}{A_{k,00}} - \underset{-2l-3}{A_{0,k0}} + \underset{2l}{\lambda}\,\underset{1}{A_k} + \dots \underset{4}{\lambda}\,\underset{2l-3}{A_k},$$

$$(15) \qquad \underset{2l+2}{A_{0,ss}^*} - \underset{2l+1}{A_{s,s0}^*} = \underset{2l}{\lambda}\,\underset{0}{A_0} + \dots \underset{4}{\lambda}\,\underset{2l-2}{A_0},$$

$$(16) \qquad \underset{2l+2}{A_0}\,\underset{0}{A_0} + \underset{2l}{A_0}\,\underset{2}{A_0} + \dots - \underset{2l+1}{A_k}\,\underset{1}{A_k} - \dots = 0.$$

Equation (13) contains expressions of order $2l+3$ in the equation $(\lambda A^\alpha)_{,\alpha} = 0$ which is an immediate consequence of (5). The only unknown function to be calculated from it is $\underset{2l+2}{\lambda}$.

Equation (14) contains expressions of the order $2l+1$ in $f^{k\alpha},_\alpha = \lambda A^k$. On the left hand we write $A_k^*$, because the addition of a gradient does not change it. Thus we may assume $A_{s,s}^* = 0$ and obtain Poisson's equations for $A_k^*$ since all expressions on the right hand side are known. $A^*$ is not $_{2l+1}$ the solution since the gradient is determined later by the normalisation condition.

Similarly equation (15) determines $A_0^*$, as a solution of a Poisson's equation $_{2l+2}$ We see in (15) that $\lambda$ already determined from (13) appears as a known $_{2l+2}$ function in (15).

Equation (16) is the normalisation condition. Since

$$(17) \qquad A_k = A_k^* + S,_k; \qquad A_0 = A_0^* + S,_0,$$
$$\phantom{(17)} \quad {}_{2l+1}\;{}_{2l+1}\;{}_{2l+1} \qquad {}_{2l+2}\;{}_{2l+2}\;{}_{2l+1}\,{}_1$$

we see that the only unknown function is $S$, determined by (16). Thus these $_{2l+1}$ steps lead to the calculation of

$$(18) \qquad\qquad \lambda,\; A_k,\; A_0$$
$$\phantom{(18)} \qquad\qquad {}_{2l+2}\;{}_{2l+1}\;{}_{2l+2}$$

and the procedure can be prolonged indefinitely.

The solution of the field equations at the same time gives the equations of motion. We interpret the right hand side of (5) according to Lorentz:

$$(19) \qquad \left\{ \begin{aligned} -\lambda A^\alpha &= \varrho_0 V^\alpha = \varrho_0 \frac{dx^\alpha}{ds} \\ \lambda^2 &= \varrho_0^2 k^{-2}. \end{aligned} \right.$$

Thus the motion and charge density are determined together with the field.

Let us now discuss the first steps of this approximation procedure. We have, as we said before:

$$(20) \qquad\qquad A_0 = \pm |k|; \qquad \lambda = 0.$$
$$\phantom{(20)} \qquad\qquad {}_0 \qquad\qquad\quad {}_2$$

Next we have $A_k$, $A_0$, satisfying Maxwell's equation for a vacuum. For $_1\quad{}_2$ the first time equation (13) appears when $l=2$:

$$(21) \qquad\qquad (\lambda A_0),_0 - (\lambda A_k),_k = 0.$$
$$\phantom{(21)} \qquad\qquad {}_4\;{}_0 \qquad\;\; {}_4\;{}_1$$

This is the equation for $\lambda$ and unlike the equations for $\lambda$ of a higher $_4$ order it is homogeneous. Therefore $\lambda$ at $t=0$ is arbitrary and determined $_4$ as a function of time through (21).

This is the theory of approximation as applied to Dirac's equations. It requires elucidation by means of simple examples, which will be given in a later note.

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# A New Approximation Method for the Meson Field Theory

by
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It has been already shown by the author [1] that the approximation method used by Einstein, Infeld, Fock and others [2] for solving many problems of classical gravitational and electromagnetic fields can also be applied to meson field theories. In the present note a general formulation of this method is attempted for use both in the classical and quantum theories.

Let us consider the equations of the meson field theory, which are all of the type

$$1) \qquad (\Box - \mu^2)\varphi = - 4\pi\Omega\delta(\vec{x} - \vec{x}_{(l)}).$$

The symbols used are:

$\varphi$ — the meson field

$\mu = \dfrac{mc}{h}$ — where $m =$ the mass of the meson, $h =$ Planck's constant, $c =$ the velocity of light

$\vec{x}_{(i)}$ — the space vector of the position of the nucleon denoted by number $(i)$.

$\delta(\vec{x})$ — three-dimensional Dirac $\delta$ function which can be defined as

$$(2) \qquad \delta(\vec{x}) = \frac{1}{(2\pi)^3}\int\limits_{-\infty}^{+\infty} e^{i\vec{k}\cdot\vec{x}} d_3 k.$$

$\Box$ — d'Alembertian operator acting on the variables $\vec{x}, t$.

$\triangle$ — Laplacian operator acting on the variables $\vec{x}$.

$\Omega$ — an operator characterizing the sources of the field. Its form depends upon the type of field and coupling.

The only assumption necessary to be made about the operator $\Omega$ is that it commutes with $\triangle$. Then we have for any function $f(\vec{x}, \vec{x}_{(i)}, t)$

$$(3) \qquad (\triangle - \mu^2)\, \Omega f(\vec{x}, \vec{x}_{(i)}, t) = \Omega(\triangle - \mu^2) f(\vec{x}, \vec{x}_{(i)}; t).$$

This assumption will be satisfied in all cases considered and we shall often make use of it.

In order to solve equation (1) we suppose that there exists an expansion of the solution $\varphi$ according to the orders of time derivatives. For instance we assume

$$(4) \qquad \varphi = \sum_{l=0}^{\infty} {}_{2l}\varphi.$$

(As regards $\Omega$ we assume it to be of the zero order. Extension to other cases is trivial). We have further an ordering rule:

$$(5) \qquad \frac{1}{c}\frac{\partial_n\varphi}{\partial t} = {}_n\dot\varphi \quad \text{is of the same order as } {}_{n+1}\varphi.$$

In the following we always put $c = 1$, thus it can be said that time differentiation raises the order by one.

We now have

$$(6) \qquad (\triangle - \mu^2)\sum {}_{2l}\varphi = -4\pi\,\Omega\,\delta(\vec{x} - \vec{x}_{(0)}) + \sum {}_{2l}\ddot\varphi$$

and after equating the terms of the same order we obtain an infinite series of simultaneous equations

$$(7) \qquad \begin{aligned} (\triangle - \mu^2)_0\varphi &= -4\pi\,\Omega\delta(\vec{x} - \vec{x}_{(i)}) \\ (\triangle - \mu^2)_2\varphi &= {}_0\ddot\varphi \end{aligned}$$

generally

$$(\triangle - \mu^2)_{2l+2}\varphi = {}_{2l}\ddot\varphi.$$

The equations of this set connect the terms differing in order by two, thus the form (4), containing only even terms, is fully justified. The sum (4) of the solutions ${}_{2l}\varphi$ of set (7) will of course also be a solution of (1).

To solve the equations (7) we can use Fourier integrals. Putting the expression for the $\delta$ function (2) in the first equation (7) and taking (3) into account, we obtain

$$(8) \qquad {}_0\varphi = \frac{1}{2\pi^2}\,\Omega\int\frac{e^{i\vec{k}\cdot\vec{r}_{(i)}}}{k^2 + \mu^2}d_3k = \Omega\,\frac{e^{-\mu\, r_{(i)}}}{r_{(i)}}.$$

The following equation

$$(9) \qquad (\triangle - \mu^2)_2\varphi = {}_0\ddot\varphi = \frac{1}{2\pi^2}\,\frac{d^2}{d\,t^2}\,\Omega\int\frac{e^{i\vec{k}\cdot\vec{r}_{(i)}}}{k^2 + \mu^2}d_3k$$

can be solved in the same manner because $(\Delta - \mu^2)$ also commutes with $\dfrac{d^2}{d t^2}$. We obtain generally in this way

(10)
$$_{2l}\varphi = (-1)^l \frac{1}{2\pi^2} \frac{d^{2l}}{d t^{2l}} \Omega \int \frac{e^{i\vec{k}\cdot\vec{r}_{(i)}}}{(k^2+\mu^2)^{l+1}} d_3 k =$$

$$= (-1)^l \frac{d^{2l}}{d t^{2l}} \Omega \frac{2}{\pi r_{(i)}} \int_0^\infty \frac{k \sin k r_{(i)}}{(k^2+\mu^2)^{l+1}} dk$$

We evaluate the integral in this expression by means of the so-called Sonine-integrals known from the theory of cylindrical functions

(11)
$$K_{\delta-\nu}(\mu r) = \frac{2^\delta \cdot \Gamma(\delta+1)}{r^\delta \cdot \mu^{\nu-\delta}} \int_0^\infty \frac{J_\nu(kr) k^{\nu+1}}{(k^2+\mu^2)^{\delta+1}} dk$$

where $K$ denotes modified Hankel functions and $J$ denotes Bessel functions If we take $\nu = \frac{1}{2}$, $\delta = l$, we have $J_{\frac{1}{2}}(kr) = \sqrt{\dfrac{2}{\pi}} \dfrac{\sin kr}{\sqrt{kr}}$ and thus we obtain

(12)
$$\frac{2^l \cdot l! \, \mu^{l-\frac{1}{2}}}{r^{l+\frac{1}{2}}} \sqrt{\frac{2}{\pi}} \int_0^\infty \frac{k \sin kr}{(k^2+\mu^2)^{l+1}} dk = K_{l-\frac{1}{2}}(\mu r) =$$

$$= \sqrt{\frac{\pi}{2\mu r}} e^{-\mu r} \sum_{n=0}^{l-1} \frac{(l-1+n)!}{n!(l-1-n)!} \cdot \left(\frac{1}{2\mu r}\right)^n.$$

We now have

(13)
$$_{2l}\varphi = (-1)^l \frac{1}{l!(2\mu)^l} \frac{d^{2l}}{d t^{2l}} \left\{ \Omega e^{-\mu r} r^{l-1} \sum_{n=0}^{l-1} \frac{(l-1+n)!}{n!(l-1-n)!} \left(\frac{1}{2\mu r}\right)^n \right\}.$$

The first three terms have the form

(14)
$$\varphi(\vec{x}, t) = {}_0\varphi + {}_2\varphi + {}_4\varphi + \ldots =$$

$$= \Omega \frac{e^{-\mu r_{(i)}}}{r_{(i)}} - \frac{1}{2\mu} \frac{d^2}{d t^2} \Omega e^{-\mu r_{(i)}} + \frac{1}{8\mu^3} \frac{d^4}{d t^4} \Omega (1 + \mu r_{(i)}) e^{-\mu r_{(i)}} \ldots$$

As can easily be shown by carrying out all the differentiations and integrations (also more directly from the asymptotic behaviour of the $k -$ Fourier transforms for $k \to \infty$), no term of our expansion will contain a singularity higher than that of the first term. Singularities higher than $1/r$ can appear solely when operator $\Omega$ is a differential operator. In any case we can say that if these higher singularities cancel in any way in the first term they will not reappear in the following terms of the expansion.

When the operator $\Omega$ contains no time differentiations, our series (4), which contains only even order time derivatives, is symmetrical with respect to the change of the time direction. It corresponds to half the sum of the

retarded and advanced potentials. There exists also an expansion with odd time derivatives, which corresponds to half the difference of the retarded and advanced potentials. But this second solution is rather unsatisfactory from the physical point of view because it contains an $e^{+\mu r}$ term tending to infinity for $r \to \infty$. In the following we shall ignore this solution.

We now deduce an important formula enabling us to operate with our series $\Sigma_{2i}\varphi$ as a whole. If we write equation (1) in the form

$$(\square - \mu^2)\varphi = -4\pi \int \delta_4(x - x') \, \Omega' \delta(\vec{x'} - \vec{x}_{(i)}) \, d_4 x' \tag{15}$$

where

$$\delta_4(x - x') = \frac{1}{(2\pi)^4} \int e^{i\vec{k}\cdot(\vec{x} - \vec{x'}) - i\nu(t - t')} \, d_3 k \, d\nu \tag{16}$$

we get

$$\varphi = \frac{1}{4\pi^3} \int \frac{e^{i\vec{k}\cdot(\vec{x} - \vec{x'}) - i\nu(t - t')}}{k^2 + \mu^2 - \nu^2} \cdot \Omega' \delta(\vec{x'} - \vec{x}_{(i)}) \, d_3 x' d_3 k \, d\nu \, dt'. \tag{17}$$

Carrying out the spatial $d_3 x'$ and $d_3 k$ integrations we obtain

$$\varphi = \frac{1}{2\pi} \int \Omega(t') \frac{e^{-r_{(i)}\sqrt{\mu^2 - \nu^2}}}{r_{(i)}(t')} \, e^{-i\nu(t - t')} \, d\nu \, dt'. \tag{18}$$

With some restrictions this can be written symbolically

$$\varphi = \int \Omega(t') \frac{e^{-r_{(i)}\sqrt{\mu^2 + \frac{d^2}{dt'^2}}}}{r_{(i)}} \cdot \delta(t - t') \, dt'. \tag{19}$$

The above formulae are very useful for discussing the influence of retardation upon the range of nuclear forces.

The classical and quantum applications of the formulae presented here will be given in a subsequent note.

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# Directional Correlations for Simultaneous Two-Quanta Processes

by

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Abstract. This note contains correlation formulae for the directions of two photons in a simultaneous process of second order (such as two-quanta emission, two-quanta absorption, Raman scattering). The formulae obtained apply to electric double dipole processes i. e. such processes where both photons are of the electric dipole type.

In the course of the calculations we obtain forms of matrix elements which are useful not only for electric dipole moment but also for a wider class of vectors.

Measurements of directional correlations of photons are admittedly possible for $\gamma$ radiation. Therefore this paper refers to a nucleus interacting with a radiation field, although the arguments equally apply to any system of charged particles.

Introduction. We shall consider an interacting system composed of the nucleus and radiation. The nucleus is taken as a system of particles, the radiation as a quantized field. We shall use the non-relativistic interaction Hamiltonian. In the Schrödinger picture it has the form:

$$(1) \quad H = H_1 + H_2, \quad \text{where} \quad H_1 = -\sum_i \frac{e_i}{m_i c} \vec{p_i} \vec{A}(\vec{x_i}), \quad H_2 = \sum_i \frac{e_i^2}{2 m_i c} \vec{A^2}(\vec{x_i}),$$

and

$$(2) \quad \vec{A}(\vec{x}) = \sqrt{\frac{\hbar c}{G}} \sum_k \sum_{l=1}^{2} k^{-\frac{1}{2}} \vec{e}_{\underset{kl}{\rightarrow}} (a_{\underset{kl}{\rightarrow}} e^{i\vec{k}\vec{x}} + \overset{*}{a}_{\underset{kl}{\rightarrow}} e^{-i\vec{k}\vec{x}}).$$

Quantities $a_{\underset{kl}{\rightarrow}}$ and $a^*_{\underset{kl}{\rightarrow}}$ are the absorption and emission operators, characterised by the wave vector $\vec{k}$ and the unit vector of linear polarization $\vec{e}_{\underset{kl}{\rightarrow}}$.

Let us now consider the representation where we have the diagonal Hamiltonian of the unperturbed system:

$$\overset{\circ}{H} |n\rangle = E_n |n\rangle.$$

[27]

The probability of transition from the state $\sum_{n'} |n'> b_{n'}(o)$ to the state $|n>$ belonging to the continuous energy spectrum per unit of time has the form (compare e. g. [1])

$$(3) \qquad \langle w_n \rangle_{av} = \frac{2\pi}{\hbar} \sum_{n'} |K_{nn'}|^2_{E_n = E_{n'}} \varrho(E_{n'}),$$

where for simultaneous processes of second order we have:

$$K_{nn'} = \sum_{n''} \frac{\langle n | H_1 | n'' \rangle \langle n'' | H_1 | n' \rangle}{E_{n''} - E_{n'}} - \langle n | H_2 | n' \rangle.$$

The averaging indicated in formula (3) pertains to the initial states $|n'>$ of nuclei interacting with radiation, where we ascribe to all states $|n'>$ appearing in the superposed state $\sum_{n'} |n'> b_{n'}(0)$ the same statistical weight.

We shall use later notations characterizing more exactly the system: nucleus + radiation without interaction:

$$(5) \quad \begin{cases} |n> = |\alpha j m N_1 N_2 \ldots N_{\vec{k}l} \ldots> = |\alpha j m> |N_1 N_2 \ldots N_{\vec{k}l} \ldots> \\ E_n = E_{\alpha j} + \sum_k \sum_{l=1}^{2} N_{\vec{k}l} \hbar ck, \quad |\vec{k}| = k, \quad \vec{k} = \vec{k}^0 k, \quad |\vec{k}^0| = 1, \end{cases}$$

here $j$ is the quantum number of total angular momentum $J$, $m$ — the magnetic quantum number defining $J_z$, $\alpha$ denotes all other labels of the states of the nucleus and finally $N_{\vec{k}l}$ are numbers of field photons with wave vectors $\vec{k}$ and linear polarization vectors $\vec{e}_{\vec{k}l}$. We assumed here that the energy levels of the nucleus are degenerated with regard to $m$.

We can now determine in more precise terms the aim of the present note, which is to find the probability per unit of time for a definite simultaneous two-quanta process involving the photons with given directions $\vec{k}_1^0$ and $\vec{k}_2^0$ and in which the nuclei of the system pass from all states with given $\alpha' j'$ to all states with given $\alpha j$. This probability is obtained after carrying out on quantities $\langle w_n \rangle_{av}$ (given by (3)) the following operations:

1. summing over the final magnetic states of the nucleus,

2. integrating over the frequencies (lenghts of wave vectors) of one of the photons. (The integration of the other photon was already performed in formula (3)),

3. summing over the directions of polarisation for both photons. In this way we get the following correlation formula for the directions of both photons:

$$(6) \qquad W_{\alpha' j' \to \alpha j}(\vec{k}_1^0, \vec{k}_2^0) = \sum_{\vec{k}_1} \sum_{l_1 l_2 = 1}^{2} \sum_m \langle w_{\alpha j m} \rangle_{av}$$

Using the formulae (3), (4), (1), (2) and the properties of the emission and absorption operators we show that formula (6), in the case when both photons belong to dipole electric radiation, has the form (compare [2])

$$
W_{\alpha'j' \to \alpha j}(\vec{k}_1^0, \vec{k}_2^0) = \sum_{l_1 l_2=1}^{2} \int dk_1 \left[ \frac{h(N_{\vec{k}_1 l_1} + \tfrac{1}{0})(N_{k_2 l_2} + \tfrac{1}{0})}{G^2 c^2 k_1 k_2} \, \varrho(k_1) \frac{\varrho(k_2)}{(\hbar c)^3} \right.
$$

$$
(7) \qquad \times \sum_{mm'} |\vec{e}_{\vec{k}_1 l_1} \cdot \widehat{\langle \alpha j m | \vec{P}\vec{P} | \alpha' j' m \rangle}_{\pm k_2} \cdot \vec{e}_{\vec{k}_2 l_2}
$$

$$
\left. + \vec{e}_{\vec{k}_2 l_2} \cdot \widehat{\langle \alpha j m | \vec{P}\vec{P} | \alpha' j' m' \rangle}_{\pm k_1} \cdot \vec{e}_{\vec{k}_1 l_1} \right|^{2}_{\pm k_2 = \frac{E\alpha'j' - E\alpha j}{\hbar c} \pm k_1}
$$

where

$$
(8) \qquad \widehat{\langle \alpha j m | \vec{P}\vec{P} | \alpha' j' m' \rangle}_{\pm k} =
$$

$$
= \sum_{\alpha'' j'' m''} \frac{\langle \alpha j m | \vec{P} | \alpha'' j'' m'' \rangle \langle \alpha'' j'' m'' | \vec{P} | \alpha' j' m' \rangle}{E_{\alpha'' j'' m''} - E_{\alpha' j' m'} \pm \hbar c k} \frac{1}{\hbar^2} (E_{\alpha j m} - E_{\alpha'' j'' m''})(E_{\alpha'' j'' m''} - E_{\alpha' j' m'}).
$$

The upper signs apply in case of emission; the lower signs, in case of absorption of the given photon: these signs can be chosen independently for both photons. According to this choice our formula refers to two-quanta emission, two-quanta absorption, or Raman scattering.

In these formulae

$$
\vec{P} = \sum_i e_i \vec{x}_i
$$

is the electric dipole moment of the nucleus and

$$
(9) \qquad \varrho(k) = \frac{G k^2 d\Omega}{(2\pi)^3}
$$

represents the density of radiation field states answering photons with given energy $\hbar c k$, direction of propagation $\vec{k}^0$ comprised within the solid angle $d\Omega$, and an arbitrary direction of linear polarization. In the formulae (7), (8) the multiplications used are: the scalar multiplication (denoted with a point) and the dyadic multiplication (without point).

We call the two-quanta process in which both photons are of electric dipole type a double-dipole electric process.

No factor derived from the second element of the interaction matrix given in (4) appears in (7). This is so because both its first expansion terms in powers of the constant $\frac{2\pi R}{\lambda}$ ($R$ is here the radius of the nucleus, $\lambda$ the radiation wave length), being the only ones comparable in order of magnitude with that of the term (8), disappear in our case: the first always

when the final $|\alpha jm>$ and the initial $|\alpha'j'm'>$ states differ, the second —
for electric double-dipole processes according to the Laporte rule. We shall
now deal with such processes.

The next step in our calculations is the evaluation of matrix elements (8),
and we will calculate as much as possible without assuming any definite
model of the nucleus.

M a t r i x   E l e m e n t s.  Let us consider the more general matrix elements

$$\langle \alpha jm | \overbrace{\vec{T}_1\,\vec{T}_2} | \alpha'j'm'\rangle_{\pm k} = \tag{10}$$

$$= \sum_{\alpha''j''m''} \frac{\langle \alpha jm|\vec{T}_1|\alpha''j''m''\rangle \langle \alpha''j''m''|\vec{T}_2|\alpha'j'm'\rangle}{E_{\alpha''j''m''} - E_{\alpha'j'm'} \pm \text{h}\,ck}\, \frac{1}{\text{h}^2}(E_{\alpha jm} - E_{\alpha''j''m''})(E_{\alpha''j''m''} - E_{\alpha'j'm'}),$$

where $\vec{T}_1$ and $\vec{T}_2$ are vectors satisfying the commutation relation:

$$[\vec{T}, \vec{J}] = -i\text{h}\vec{T}\times\breve{I}. \tag{11}$$

$\vec{J}$ is here the total angular momentum, $\breve{I}$ the unit dyad (the »v« cap sign
denotes dyads).

The relation (11) is satisfied among others by vectors: $\vec{J}, \vec{x}_i, \vec{p}_i$ and
all their linear combinations and vector products such as the dipole moments:
electric $\vec{P}$ and magnetic $\vec{M}$ (compare [3]).

After using the well known formulae for matrix elements $\langle \alpha jm|\vec{T}|\alpha'j'm'\rangle$
(compare [3]) and after performing tedious summations (compare similar
calculations in [4]) we get the results given in Table I.

We have used there the following notations:

$$\breve{K}(0) = \sqrt{\tfrac{2}{3}}(\vec{k}\vec{k} - \tfrac{1}{2}\vec{i}\vec{i} - \tfrac{1}{2}\vec{j}\vec{j}), \qquad \breve{K}(\pm 1) = \tfrac{1}{2}[\vec{k}\vec{i} + \vec{i}\vec{k} \pm i(\vec{k}\vec{j} + \vec{j}\vec{k}), \tag{12}$$
$$\breve{K}(\pm 2) = \tfrac{1}{2}[\vec{i}\vec{i} - \vec{j}\vec{j} \pm i(\vec{i}\vec{j} + \vec{j}\vec{i}),$$

$$\breve{D}(0) = \tfrac{1}{2}(\vec{i}\vec{j} - \vec{j}\vec{i}), \qquad \breve{D}(\pm 1) = \pm\tfrac{1}{2}[\vec{i}\vec{k} - \vec{k}\vec{i} \pm i(\vec{j}\vec{k} - \vec{k}\vec{j})] \tag{13}$$

and symbols $\langle \alpha j \overbrace{:\,T_1 T_2\,:}\,\alpha'j'\rangle_{\pm k}$, $\langle \alpha j \overbrace{:\,T_1\cdot T_2\,:}\,\alpha'j'\rangle_{\pm k}$, $\langle \alpha j \overbrace{:\,T_1\times T_2\,:}\,\alpha_1 j'\rangle_{\pm k}$ denot-
ing coefficients built up from quantities

$$\sum_{\alpha''} \frac{\langle \alpha j\,:\,T_1\,:\,\alpha''j''\rangle \langle \alpha''j''\,:\,T_2\,:\,\alpha'j'\rangle}{E_{\alpha''j''} - E_{\alpha'j'} \pm \text{h}\,ck}(E_{\alpha j} - E_{\alpha''j''})(E_{\alpha''j''} - E_{\alpha'j'})$$

in the same way as the coefficients in matrix elements $\langle \alpha jm | \vec{T}_1\,\vec{T}_2 | \alpha'j'm'\rangle$
$\langle \alpha jm | \vec{T}_1\cdot\vec{T}_2 | \alpha'j'm'\rangle$, $\langle \alpha jm | \vec{T}_1\times\vec{T}_2 | \alpha'j'm'\rangle$ are formed from quantities

$$\sum_{\alpha''} \langle \alpha j\,:\,T_1\,:\,\alpha''j''\rangle \langle \alpha''j''\,:\,T_2\,:\,\alpha'j'\rangle$$

(compare [3] and also [5]).

The quantities $\langle \alpha j : T : \alpha'' j'' \rangle$ are generally unknown. For their evaluation we must know the eigenfunctions of the nucleus.

Correlation Formulae. Inserting the matrix elements given in Table I in (7) and carrying out the rather tedious calculations we get finally the correlation formulae collected in Table II, where $\theta$ denotes the angle between the directions of both photons.

In these formulae we dropped the common factor independent of photon directions, and have in this way obtained the relative probabilities.

In table II we use the following notations

$$
\begin{cases}
I_1(\alpha j; \alpha' j') = \\
\quad = \int dk_1 \left[ \frac{h(N_{\vec{k}_1} + \tfrac{1}{0})(N_{\vec{k}_2} + \tfrac{1}{0})}{Gc^2 k_1 k_2} \varrho(k_1) \frac{\varrho(k_2)}{(\hbar c)^3} |\langle \alpha j : \widehat{PP} : \alpha' j' \rangle_{\pm k_2} + \langle \alpha j : \widehat{PP} : \alpha' j' \rangle_{\pm k_1}|^2 \right]_{\pm k_2 = \frac{E_{\alpha' j'} - E_{\alpha j}}{\hbar c} \mp k_1} \\[4mm]
I_2(\alpha j; \alpha' j') = \\
\quad = \int dk_1 \left[ \frac{h(N_{\vec{k}_1} + \tfrac{1}{0})(N_{\vec{k}_2} + \tfrac{1}{0})}{Gc^2 k_1 k_2} \varrho(k_1) \frac{\varrho(k_2)}{(\hbar c)^3} |\langle \alpha j : \widehat{P \cdot P} : \alpha' j' \rangle_{\pm k_2} + \langle \alpha j : \widehat{P \cdot P} : \alpha' j' \rangle_{\pm k_1}|^2 \right]_{\pm k_2 = \frac{E_{\alpha' j'} - E_{\alpha j}}{\hbar c} \mp k_1} \\[4mm]
I_3(\alpha j; \alpha' j') = \\
\quad = \int dk_1 \left[ \frac{h(N_{\vec{k}_1} + \tfrac{1}{0})(N_{\vec{k}_2} + \tfrac{1}{0})}{Gc^2 k_1 k_2} \varrho(k_1) \frac{\varrho(k_2)}{(\hbar c)^3} |\langle \alpha j : \widehat{P \times P} : \alpha' j' \rangle_{\pm k_2} - \langle \alpha j : \widehat{P \times P} : \alpha' j' \rangle_{\pm k_1}|^2 \right]_{\pm k_2 = \frac{E_{\alpha' j'} - E_{\alpha j}}{\hbar c} \mp k_1}
\end{cases}
\tag{4}
$$

We also assume that the initial distribution of photons among polarisations is random i. e. $N_{\vec{k}_l} = N_{\vec{k}}$. This occurs, for instance, in the case of two-quanta spontaneous emission (then $N_{\vec{k}_l} = 0$).

The factors $I_s(\alpha j; \alpha' j')$ $(s = 1, 2, 3)$ are generally unknown. For their evaluation we must know again the eigenfunctions of the nucleus.

Estimating the order of magnitude of factors $I_s$, with the assumption that the nucleus passes only through one intermediate state $|\alpha'' j'' m''\rangle$ (compare [6]) we obtain

$$
\frac{I_3}{I_1} \sim 1, \quad \frac{I_2}{I_1} \sim 1. \tag{15}
$$

Final Remarks. The simultaneous and successive processes of second order differ by the existence in the last case of a real intermediate state through which the nucleus passes.

However, our formulae given in Table II are identical with Hamilton's [7] for directional correlations of successive emission of two dipole quanta $\gamma$ in cases when, in the simultaneous emission, only virtual intermediate states with a single value of $j''$ exist (according to the selection rules). In these, unknown factors $I_s$ do not appear in Table I. In other cases of simultaneous emission there are intermediate virtual states with different values of $j''$ and it is to be expected that there are differences in correlation formulae for simultaneous and successive emission.

## TABLE I

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j m\rangle_{\pm k} = \breve{K}(0)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j\rangle_{\pm k} \cdot \tfrac{1}{\sqrt{6}}[3m^2 - j(j+1)]$$
$$+ \tfrac{1}{3}\breve{L}\langle \alpha j | \overrightarrow{T_1 \cdot T_2} | \alpha' j\rangle_{\pm k} + \breve{D}(0)\langle \alpha j : T_1 \times T_2 : \alpha' j\rangle_{\pm k} \cdot m$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j - 1, m\rangle_{\pm k} = \breve{K}(0)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j - 1\rangle_{\pm k} \cdot m\sqrt{\tfrac{3}{2}(j-m)(j+m)}$$
$$- \breve{D}(0)\langle \alpha j : T_1 \times T_2 : \alpha' j - 1\rangle_{\pm k}\sqrt{(j-m)(j+m)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j + 1, m\rangle_{\pm k} = \breve{K}(0)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j + 1\rangle_{\pm k} \cdot m\sqrt{\tfrac{3}{2}(j-m+1)(j+m+1)}$$
$$- \breve{D}(0)\langle \alpha j : T_1 \times T_2 : \alpha' j + 1\rangle_{\pm k}\sqrt{(j-m+1)(j+m+1)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j - 2, m\rangle_{\pm k} = \breve{K}(0)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j - 2\rangle_{\pm k}\sqrt{\tfrac{3}{2}(j-m)(j+m)(j-m-1)(j+m-1)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j + 2, m\rangle_{\pm k} = \breve{K}(0)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j + 2\rangle_{\pm k}\sqrt{\tfrac{3}{2}(j-m+1)(j+m+1)(j-m+2)(j+m+2)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j m \pm 1\rangle_{\pm k} = \breve{K}(\pm 1)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j\rangle_{\pm k \frac{1}{2}}(2 \pm 1)\sqrt{(j \mp m)(j \pm m + 1)}$$
$$+ \breve{D}(\pm 1)\langle \alpha j : T_1 \times T_2 : \alpha' j\rangle_{\pm k \frac{1}{2}}\sqrt{(j \mp m)(j \pm m + 1)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j - 1, m \pm 1\rangle_{\pm k} = \breve{K}(\pm 1)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j - 1\rangle_{\pm k \frac{1}{2}}(j \pm 2m + 1)\sqrt{(j \pm m)(j \pm m + 1)}$$
$$- \breve{D}(\pm 1)\langle \alpha j : T_1 \times T_2 : \alpha' j - 1\rangle_{\pm k}\sqrt{(j \mp m)(j \mp m - 1)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j + 1, m \pm 1\rangle_{\pm k} = \breve{K}(\pm 1)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j + 1\rangle_{\pm k \frac{1}{2}}(j \mp 2m)\sqrt{(j \pm m + 1)(j \pm m + 2)}$$
$$- \breve{D}(\pm 1)\langle \alpha j : T_1 \times T_2 : \alpha' j + 1\rangle_{\pm k \frac{1}{2}}\sqrt{(j \pm m + 1)(j \pm m + 2)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j - 2m \pm 1\rangle_{\mp k} = \breve{K}(\pm 1)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j - 2\rangle_{\pm k}(\pm)\sqrt{(j - m)}\sqrt{(j \mp m)(j \mp m - 1)(j \mp m - 2)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j + 2m \pm 1\rangle_{\mp k} = \breve{K}(\pm 2)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j + 2\rangle_{\pm k}(\mp)\sqrt{(j - m + 1)}\sqrt{(j \mp m)(j \mp m + 1)(j \pm m + 2)(j \pm m + 3)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j m \pm 2\rangle_{\mp k} = \breve{K}(\pm 2)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j\rangle_{\pm k \frac{1}{2}}\sqrt{(j \mp m)(j \mp m - 1)(j \pm m + 1)(j \pm m + 2)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j - 1m \pm 2\rangle_{\mp k} = \breve{K}(\pm 2)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j - 1\rangle_{\mp k}\tfrac{1}{2}\sqrt{(j \mp m)(j \mp m - 1)(j \mp m - 2)(j \pm m + 1)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j + 1m \pm 2\rangle_{\mp k} = \breve{K}(\pm 2)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j + 1\rangle_{\pm k}(\pm)\tfrac{1}{2}\sqrt{(j \mp m)(j \pm m + 1)(j \pm m + 2)(j \pm m + 3)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j - 2m \pm 2\rangle_{\mp k} = \breve{K}(\pm 2)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j - 2\rangle_{\pm k \frac{1}{2}}\sqrt{(j \mp m)(j \mp m - 1)(j \mp m - 2)(j \mp m - 3)}$$

$$\langle \alpha j m \,|\, \overrightarrow{\overset{\rightarrow}{T_1}\overset{\rightarrow}{T_2}} \,|\, \alpha' j + 2m \pm 2\rangle_{\mp k} = \breve{K}(\pm 2)\langle \alpha j : \overrightarrow{T_1 T_2} : \alpha' j + 2\rangle_{\pm k \frac{1}{2}}\sqrt{(j \pm m + 1)(j \pm m + 2)(j \pm m + 3)(j \pm m + 4)}$$

## TABLE II

$$W_{\alpha'j\pm2\,\to\,\alpha j}(\theta) = 1 + \frac{1}{13}\cos^2\theta$$

$$W_{\alpha',\,j-1\,\to\,\alpha j}(\theta)_{(j\neq1)} = 1 + \frac{1}{13}\cos^2\theta + \frac{I_3(\alpha j;\;\alpha'j-1)}{I_1(\alpha j;\;\alpha'j-1)}\cdot\frac{15}{13}\cdot\frac{1}{(j-1)(j+1)}\left(1-\frac{1}{3}\cos^2\theta\right)$$

$$W_{\alpha'0\,\to\,\alpha1}(\theta) = 1 - \frac{1}{3}\cos^2\theta$$

$$W_{\alpha'j+1\,\to\,\alpha j}(\theta)_{(j\neq0)} = 1 + \frac{1}{13}\cos^2\theta + \frac{I_3(\alpha j;\;\alpha'j+1)}{I_1(\alpha j;\;\alpha'j+1)}\cdot\frac{15}{13}\cdot\frac{1}{j(j+2)}\left(1-\frac{1}{3}\cos^2\theta\right)$$

$$W_{\alpha'j\,\to\,\alpha0}(\theta) = 1 - \frac{1}{3}\cos^2\theta$$

$$W_{\alpha'j\,\to\,\alpha j}(\theta)_{(j\neq0,\,\frac12)} = 1 + \frac{1}{13}\cos^2\theta + \frac{I_3(\alpha j;\;\alpha'j)}{I_1(\alpha j;\;\alpha'j)}\frac{15}{13}\cdot\frac{3}{4}\cdot\frac{1}{(j-\frac12)(j+\frac32)}\left(1-\frac{1}{3}\cos^2\theta\right) +$$
$$+ \frac{I_2(\alpha j;\;\alpha'j)}{I_1(\alpha j;\;\alpha'j)}\frac{15}{13}\cdot\frac{1}{3}\cdot\frac{1}{(j-\frac12)(j+\frac12)(j+\frac32)}(1+\cos^2\theta)$$

$$W_{\alpha'\frac12\,\to\,\alpha\frac12}(\theta) = 1 - \frac{1}{3}\cos^2\theta + \frac{I_2(\alpha\frac12;\;\alpha'\frac12)}{I_3(\alpha\frac12;\;\alpha'\frac12)}\frac{4}{9}\cdot\frac{1}{j(j+1)}(1+\cos^2\theta)$$

$$W_{\alpha'0\,\to\,\alpha0}(\theta) = 1 + \cos^2\theta$$

Actually a superficial estimation in the case of the simultaneous emission with the transition $\alpha'2 \to \alpha 2$ gives the correlation function $1 + \frac{1}{4}\cos^2\theta$ and for the successive emission $\alpha'2 \to \alpha''1 \to \alpha2$ it has the form $1 + \frac{1}{133}\cos^2\theta$

Especially interesting is the case of a two-quanta process with the transition $\alpha'0 \to \alpha 0$, strictly forbidden for one-quantum emission and absorption (compare [6] and [8]). We have here »pure« experimental conditions for investigation of the two-quanta process.

The initial idea of the present note is due to Prof. Rubinowicz to whom I am indebted for his kind interest in my work.

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# Nonlinear Electrodynamics and Elementary Laws

by

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1. The nonlinear electrodynamics developed by Born and Infeld [1] was built up by means of certain Lagrange functions the choice of which was, however, quite arbitrary. It is well known that the introduction of nonlinearity to the theory gives us the possibility of obtaining finite Coulomb energy, stability of the free electron (Laue's theorem), i. e. a logical development of the field mass theory.

The fundamental difficulty in the theory, if we depart from linearity, is the arbitrariness in the choice of the Lagrangian, as the relativistic invariance and gauge invariance alone are not sufficient to determine the Lagrangian.

In the case of fields to which the principle of superposition applies (e. g. fields which satisfy linear equations) W. Rubinowicz [2] pointed out the significant role played by spherically symmetrical solutions, by mean of which other solutions can be obtained.

The purpose of this note is to show that the position in the case of nonlinear electrodynamics is similar. The assumption that we know an "elementary law" of this theory — analogous to the Coulomb law enables us to find its Lagrangian, and hence the field equations. This result may be helpful in the search for additional assumptions which could define the form of the Lagrangian unambiguously.

2. If we assume that the equations of electrodynamics are of the II-nd order in the potentials $A_\alpha$ (the el.-mag. field is defined as $f_{\alpha\beta} = A_{\beta,\alpha} - A_{\alpha,\beta}$), then since the Lagrangian is a scalar function, this function must depend only on the two invariants:

$$(1) \qquad F = \tfrac{1}{4} f_{\alpha\beta} f^{\alpha\beta} = \tfrac{1}{2}(\vec{B^2} - \vec{E^2}),$$

$$(2) \qquad G^2 = (\tfrac{1}{4} f_{\alpha\beta} f^{*\alpha\beta})^2 = (\vec{E} \cdot \vec{B})^2.$$

Invariant $A_\alpha A^\alpha$ is eliminated by the postulated gauge invariance, as the potentials cannot appear in field equations explicitly. Thus the Lagrangian is some function of $F$ and $G^2$: $L = L(F, G^2)$.

If we take into consideration only the field produced by the point charge $e$, which rests at the origin of the coordinate system, then assuming $\vec{B} = 0$, $\vec{E} = -\nabla\varphi(r)$, we obtain from the variational principle:

$$(3) \qquad \delta \int r^2 dr \, [L(-\varphi'^2/2, 0) - 4\pi e \, \vec{\delta(r)} \, \varphi] = 0$$

the equation for $\varphi(r)$ as:

$$(4) \qquad \frac{1}{r^2} \frac{d}{dr} r^2 \left(\frac{dL_0}{dF}\right)_{F=-\varphi'^2/2} \varphi' = -4\pi e \, \vec{\delta(r)}$$

(We define $L_0(F) = L(F, 0)$).

The solution of eq. (4) is:

$$(5) \qquad \varphi' \left(\frac{dL_0}{dF}\right)_{F=-\varphi'^2/2} = -e/r^2.$$

From this equation certain conclusions may be drawn. $p = \varphi'(r)$ is analogous to the Coulomb law in the nonlinear theory. (If $L_0 = F$ — linear electrodynamics — then $p = e/r^2$ is the intensity of the electrostatic field produced by a point charge). Equation (5) gives $r^2$ as a definite function of $p$. The solution of (5) with respect to $p$ can however give, not one, but many branches of the function $p(r)$. It seems physically necessary to postulate from $L_0(F)$ such a structure that only one function $p(r)$ could by obtained from (5); otherwise many electrostatic fields — none of which would be preferable to any other — could be attributed to one charge.

From (5) we see also that if we take $p$ corresponding to the positive charge — $p_+$ — the sign before $e$ must be changed in (5) — the field in this case will differ only by the sign from $p_-$ corresponding to the negative charge (the left hand part of (5) is an even function of $p$).

We emphasise also the fact, which follows from the whole discussion, namely, that the form of the dependence of $L$ on $G^2$, does not influence the shape of the function $p(r)$.

3. Let us now assume that we do not have the function $L_0(F)$, but that we know instead the function $p = f(r)$, which is monotonic for $0 \leqslant r \leqslant \infty$, so that $r^2 = g(p)$ is a function defined without ambiguity. We assume also (which is physically reasonable) that $p < 0$ for $0 \leqslant r \leqslant \infty$. Since in (5) $F = -p^2/2 \quad dF = -p \, dp; \quad p = -\sqrt{-2F}$, therefore (5) can be written as

$$dL_0 = e \frac{dp}{r^2}$$

and hence

$$(6) \qquad L_0(F) = \int^{-\sqrt{-2F}} \frac{dp}{g(p)} + C.$$

Therefore if $p = f(r)$ is given, we can define $L_0(F)$ with accuracy up to unimportant additive constants.

We see, therefore, that if $L$ is limited to dependence on $F$ alone, then the "elementary law", $p(r)$, defines the Lagrangian unambiguously. Field equations for the general fields can now be obtained by the conventional variational principle. In this case all solutions of our field equations are fixed by the "elementary law".

The assumptions therefore of: 1) relativistic covariance, 2) gauge invariance, 3) second order for field equations, together with the "elementary law" define the field equations under the condition that $L$ is independent of $G^2$.

If in (6) we take Coulomb's law as $p$, then automatically we get $L_0 = F$, i. e. Maxwell's theory; this assumption leads also to the Lagrangian of the linear theory.

If, therefore, we wish to obtain a certain satisfactory nonlinear electrodynamics without ambiguities, it seems necessary to find some reasonable physical assumptions leading to the "elementary law". The eq. (6) points out the important role of the Coulomb law, or its "nonlinear" analogue as an independent postulate in the theory.

From the "elementary law" we cannot deduce anything about the dependence of $L$ on $G^2$. We note, however, that certain purely formal reasons (3) lead to the assumption that $L$ as a function of $F$ and $G$ must be a harmonic function $(L_{FF} + L_{GG} = 0)$ which together with a given $p(r)$ and hence $L(F, 0)$, should give us $L(F, G^2)$.

There is no reason for $L$ in nonlinear theory to be dependent on $F$ only. The dependence of $L$ on $G^2$ allows us to describe clasically the scattering of light by light, connected with pair creations.

It should be noted further that with help of (6) we can build a Lagrangian for nonlinear theory such that this theory will have its "elementary law" identical with the elementary law of a theory with higher derivatives.

We may also add that the argument for explicitly introducing potentials in the theory, as is done in mesodynamics, originates in the desire to obtain short range forces of the Yukawa type.

Forces of such a kind can be also obtained from the non linear gauge invariant theory: if we take $p(r) = g \dfrac{d}{dr} e^{-\mu r}/r$, then the corresponding Lagrangian can be obtained from (6).

4. Knowing that the "elementary law", $p(r)$, defined $L_0(F)$, it is interesting to investigate which $p(r)$ are satisfactory from the point of view of the field mass hypothesis, in which we want to obtain the finite electrostatic energy of a field produced by a point charge, in order to compare it with $mc^2$; to obtain the electron stability we postulate also that the space-integral of the diagonal elements of the energy-momentum tensor all vanish (Laue's theorem).

If $T_{\alpha\beta}$ is the energy-momentum tensor, then in the case which interests us, namely the electrostatic field of a point charge, we easily obtain:

$$(7) \qquad I = \int\limits_{\infty} d\tau_{(3)} T_{11} = \int\limits_{\infty} d\tau_{(3)} T_{22} = \int\limits_{\infty} \tau_{(3)} T_{33} = -\,^2/_3 e\,(\omega\,(\infty) - \omega\,(0)),$$

$$(8) \qquad W = \int\limits_{\infty} d\tau_{(3)} T_{00} = -\,^2/_3 e \int\limits_{0}^{\infty} p(r)\,dr - I,$$

when

$$\omega(r) = r^3 \left[ \int\limits^{r} p(r)\frac{dr}{r^3} - C/2 \right],$$

$C$ is an additive constant from (6).

If we want $p(r)$ for large $r$ to have the shape $p(r) = -e/r^2 + O(1/r^3)$ (in other words asymptotic Coulomb's behaviour), then it is easy to see that $\omega(\infty) = 0$, if we choose $C$ equal to zero $(C \neq 0 \to \omega(\infty) = \infty)$. Conversely, if we want $\omega(\infty) = 0$, then if $p(\frac{1}{z})$ expands near $z = 0$ into a Laurent series, then the principal part of this series must vanish, and the analytical part must begin with $z^2$; $C$ must be equal to zero.

Suppose $\omega(\infty) = 0$; then if $I = 0$, we must have $\omega(0) = 0$. This implies that if $p(r)$ can be expanded in a Laurent series nearly to $r = 0$ the principal part of this series must vanish, and hence $\lim\limits_{r \to 0} p(r) = p_0$ must be a finite number.

If $I = 0$, then in order that [4]*), $W = -\,^2/_3 e \int\limits_{0}^{\infty} p(r)dr = \,^2/_3 e\,\varphi(0)$ be finite it is sufficient to assume that $p$ which for large $r$ behaves as $-e/r^2$, and is analytical for $r = 0$, should be a monotonic function. (This assumption has been used in the derivation of (6)).

Concluding, we see that $p(r)$ of the form: $p(r) = -e/r_0^2\,G(r/r_0)$ would be physically reasonable, where $G(q)$ is a monotonic function of $q$, which for $0 \leqslant q \ll 1$ is $G(q) = 1 + 0(q)$, and for $q \gg 1$, $G(q) = 1/q^2 + 0(1/q^3)$.

If we find from (6) $L_0(F)$ for $P = -e/r_0^2\,G(r/r_0)$, where $G(q)$ satisfies the conditions specified above, we can prove that $\lim\limits_{r_0 \to 0} L_0 = F$; these conditions therefore guarantee the Maxwellian limit for the nonlinear theory.

It is interesting to take for $G(q)$ a number of simple assumptions; equating the corresponding $W$ and $mc^2$, we get $r_0$ which is always of the same order of magnitude. (E. g. for $G = \dfrac{1}{\sqrt{1+q^4}}$, $G = \dfrac{1}{1+q^2}$, $G(q) = th\,1/q^2$, $G(q) = \dfrac{1}{(1+q)^2}$, and so on).

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I should like to thank Professors L. Infeld and W. Rubinowicz for their kind interest in this work.

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# Radioactivité d'un groupe de phosphorites polonais I

par

## S. PIEŃKOWSKI

Pour l'étude de propriétés radioactives des minerais les phosphorites *)
présentent un intérêt particulier et cela tant du point de vue de leur origine
et de leur évolution que du point de vue de l'analyse de migration et de
localisation des substances radioactives. Dans cette note je résume les résul-
tats des mesures d'un groupe de phosphorites d'origines différentes.

Méthode de mesure. Comme il était à prévoir que la radioactivité
des phosphorites serait faible, on utilisait soit la méthode des compteurs
Geiger-Mueller convenablement appropriée, soit celle des émulsions nuclé-
aires, soit les deux conjointement.

Dans la première une pastille (de 14 mm de diamètre et de 3 mm
d'épaisseur), formée de l'échantillon de phosphorite finement pulvérisé, servait
de source de rayonnement. Elle était placée à une distance de 0·4 mm de
la fenêtre en mica du compteur. La fenêtre d'une épaisseur de 2·4 mg/cm²
laissait passer les rayons $\alpha$. Les impulsions étaient convenablement enregi-
strées.

La différentiation des impulsions dues aux rayons $\alpha$ de celles données
par les rayons $\beta$ et $\gamma$ pouvait être obtenue par introduction de $50\mu$ d'Al.

Les impulsions du compteur étaient convenablement enregistrées au
moyen d'un scaler.

Ces mesures ont été reliées au rayonnement d'une substance étalon
dont la concentration en uranium a été déterminée par la méthode de dénom-
brement de toutes les particules $\alpha$ émises pendant l'unité de temps dans
l'angle $4\pi$ par une quantité connue de cette substance à l'état de poudre
fine placée entre deux couches d'émulsion nucléaire.

Ces données permettaient de calculer la concentration en uranium des
échantillons étudiés. La connaissance de cette valeur permet de calculer les
quantités de tous les autres éléments de deux familles radioactives.

Les valeurs de $C(U)$ ainsi obtenues sont correctes à condition que les
produits étudiés contiennent des éléments radioactifs des familles d'uranium

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*) On appelle souvent ces formations: phosphates de chaux. Voir [1].

et de thorium en équilibre; le rapport $C(Th)/C(U)$ est sensiblement le même pour tous les échantillons et leur composition chimique moyenne diffère peu. Dans le cas des phosphorites étudiés ici toutes ces conditions sont suffisamment remplies dans les limites de précision valables. Remarquons toutefois qu'il est très souvent difficile de dire jusqu'à quel degré l'échantillon étudié représente les propriétés moyennes du milieu, étant donné son hétérogénéité plus ou moins élévée mais toujours appréciable. L'étude de la distribution des substances radioactives dans le minerai montre toute l'importance de ce facteur. Cependant, dans les cas étudiés ici les séries de mesures se rapportant au même prélèvement ne différaient que de 5 à 8%. Il n'est pas douteux que les échantillons provenant de différents points d'une même

TABLEAU I

| Echantillon | Etage géologique | Age en $10^6$ ans | $C(U)$ unités arbitr. |
|:---:|:---:|:---:|:---:|
| 1 | Cambrien moy. | 400 | 3·7 |
| 2 | „ „ | 370 | 9·4 |
| 3 | Ordiwikien sup. | 350 | 5·3 |
| 4 | Cenomanien inf. | 100 | 63·0 |
| 5 | „ „ | 100 | 46·0 |
| 6 | „ moy. | 95 | 47·6 |
| 7 | „ „ | 95 | 47·8 |
| 8 | Maestrichtien | 75 | 138·7 |
| 9 | Crétacé sup. | 60 | 132·5 |

couche montrent des différences plus notables. (Il est à noter toutefois que les échantillons numérotés 5, 6, 7 dans le tableau I ont été prélevés dans les couches analogues de niveaux géologiques proches mais en des points distants de plus de 200 km. Leurs concentrations en uranium ne diffèrent cependant que de 4% au plus).

Résultats de mesures. L'étude de l'activité des échantillons de provenances différentes a montré que tous ces phosphorites contiennent des substances radioactives, mais que leurs activités diffèrent sensiblement.

En cherchant à obtenir une série d'échantillons provenant de formations géologiques d'âge différent, j'ai pu réunir les phosphorites de neuf provenances différentes allant du niveau cambrien (env. $400 \cdot 10^6$ ans) au crétacé supérieur (env. $60 \cdot 10^6$ ans). Je dois leur choix à mes collègues M. le Prof. J. Samsonowicz et M. le Prof. R. Kozłowski, auxquels je tiens à adresser mes remerciements les plus cordiaux.

Le tableau ci-dessus donne la liste des phosphorites typiques étudiés, leur localisation dans les niveaux géologiques ainsi que l'estimation approximative de leur âge. La dernière colonne indique la valeur $C(U)$ de concentration en uranium en unités arbitraires.

Ces nombres montrent que les phosphorites examinés ici possèdent une radioactivité appréciable, variable dans des limites relativement larges (de 3·7 à 138·7). Mais en outre nous voyons une tendance nettement marquée de variation de l'activité avec l'âge du minerai.

Les phosphorites très âgés sont faiblement radioactifs. Cependant leur activité augmente progressivement pour les formations moins âgées. La courbe de la Fig. 1 montre la variation de la concentration $C(U)$ en uranium en fonction de l'âge attribué au niveau géologique. L'existence d'une telle relation entre la teneur des substances radioactives et l'âge du phosphorite paraît être des plus intéressantes. Elle peut être due soit aux conditions régnant lors de la formation du dépôt, soit au mode de son évolution. Plusieurs hypothèses peuvent être suggérées pour nous rendre compte de l'allure de cette courbe. Mais il me semble qu'il est trop tôt de passer aux interprétations fondées. Les recherches en cours promettent des données nouvelles.
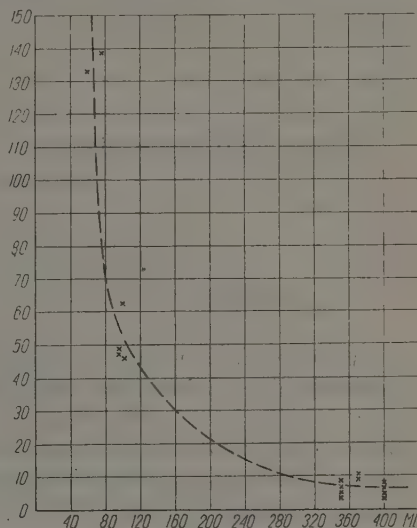


Fig. 1

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# Delayed Disintegration of a Heavy Fragment Emitted in Nuclear Explosion

by

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Introduction. A remarkable coincidence of two events recorded in a photographic emulsion was recently observed in this laboratory. It occurred in a G 5 plate, 600 $\mu$ thick, which had been exposed at high altitude (85.000 feet)*) to cosmic radiation, and concerns two stars marked $A$ and $B$ (Fig. 1). The centre of the star $B$ coincides with the end of the track of a heavy fragment $f$, ejected from star $A$. If this coincidence is not accidental, it must be considered as an example of delayed disintegration of a heavy fragment. The probability of such a coincidence being very small, we thought it might be of interest to analyse the case more closely. It is clear, of course, that any conclusions drawn from a single observation should be treated with due caution.

Analysis. The disintegration referred to as star $A$ represents the effect of a high energy interaction, presumably between a singly charged particle and a bromine or silver nucleus. The disintegration referred to as star $B$ seems to be a case of delayed decay of a heavy fragment ejected from the star $A$.

Following the nomenclature of Brown et al. [1], star $A$ may be described as a star of type $21 + 18\,p$. The track $p$ (see Fig. 1) — the only minimum track in the upper hemisphere, the direction of which coincides approximately with the direction of the »centre of gravity« of the emitted shower particles — apparently represents the incident particle, the primary of the disintegration $A$. Scattering measurements do not allow direct energy evaluation (lenght about 2 mm) but are not inconsistent with this assumption. Using statistical data, Camerini et al. [2], Daniel et al. [3] we estimate the energy of the primary to be about 30 Mev. Energy measurements on longer tracks of shower particles are also in agreement with this assumption.

From the analysis of the black and grey tracks of star $A$ we could identify nine $\alpha$-particles, one heavy fragment and eleven singly charged

*) We are indebted to Professor C. F. Powell for the oportunity of exposing the plates in a balloon flight and processing them in the H. H. Wills Laboratory at Bristol.

particles, which, as no slow mesons were detected, represent protons, deuterons or tritons. A comparison of the shape of the track $f$ with those of other multiply charged particles stopping in the emulsion enables us to make a rough estimate of the charge of the fragment $f$ — the probable value being about 12.
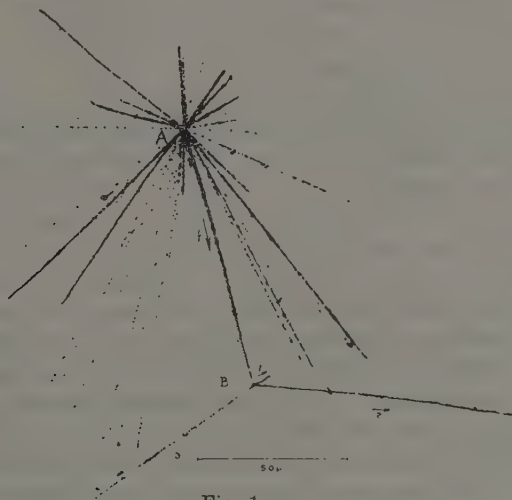


Fig. 1

The initial kinetic energy of the fragment $f$, estimated from its range ($90\,\mu$) and charge, Perkins [4], is of the order of 150 Mev.

The heavy fragment seems to stop in the emulsion exactly in the centre of star $B$. Its final energy, as deduced from the breadth of the end part of its track, is very small and certainly much less than that necessary to produce the star $B$. Hence we may estimate the time of flight of the fragment as being of the order of $10^{-11}$ sec.

The results of the analysis of star $B$, which is a low energy four-prong star, are given in the table below:

| Track N | Range | Grain density | Identity | Energy of proton |
|---------|-------|---------------|----------|------------------|
| 1 | $9\,\mu$ | black | $p, d, t$ or $\alpha$ | ·7 Mev. |
| 2 | $123\,\mu$ | black | $p, d, t$ or $\alpha$ | 16 Mev. |
| 3 | — | $3 \cdot 7 \pm \cdot 2$ | $\pi\, p, d, t$ | 82 Mev. |
| 4 | $< 2\,u$ | black | recoil | — |

Taking into account the binding energy of the emitted particles, we get for the total energy released in event $B$ a value equal to, or greater than 120 Mev. However we may expect that some neutrons should be

emitted as well. In this case the total internal energy of the fragment should be at least 140 Mev.

The estimation of the probability of chance coincidence between the end of track $f$ and the centre of star $B$ in the problem under consideration was calculated from the average star density in the exposed plate and local increase in the radiation density, due to the proximity of star $A$, on the one hand, and the known optical resolution of the microscope, on the other. This probability is certainly less than $10^{-7}$.

C o n c l u s i o n. Excluding the explanation that the event was due to a coincidence, we are left with alternative possibilities: stars of this type might be considered either as due to an interaction between heavy fragments and nuclei of the emulsion or as a spontaneous decay of such fragments (5, 6, 7). It is clear, however, that in our case the first interpretation is incorrect (small, if not zero, final kinetic energy of the fragment). The fragment must have been emitted with high internal energy (at least 120 Mev, and probably more than 140 Mev) and must have remained stable against $\gamma$-transitions and the emission of particles during a time exceeding $10^{-11}$ sec. This makes it difficult to interpret the case in terms of a highly excited state of the nucleus. It might be supposed that the explosion was due to a $\pi^-$-meson capture at $B$, the meson being picked up on the Coulomb orbit of $f$ at $A$. It would be a kind of delayed $\sigma$-star. What this supposition is worth depends on the probabilities both of the picking-up process and of the capture. Attractive as it is from the point of view of energy considerations, it seems to us rather unlikely.

Another attempt to find an explanation of the event might be looked for in connection with the concept of the heavy neutral $V_1^0$ — particle considered as a nucleon in an excited state with a mean life-time of about $10^{-10}$ sec. We assume that an unstable particle identical with $V_1^0$ (or of similar type) might exist not only as a free particle but also in a bound state within the nucleus. If the $f$-fragment was formed with such an excited particle among its nucleons, this would possibly account for the delayed disintegration as well as for the observed release of energy.

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# The Scattering of Slow Neutrons by Liquids
# I. Experiments with $CH_3OH$ and $CH_3I$

by
## J. A. JANIK

*Communicated by H. NIEWODNICZAŃSKI at the meeting of September 22, 1952*

The scattering of slow neutrons by molecular gases is described by the theory of Sachs and Teller [1]. This theory states that if the energy of a neutron is low in comparison to the vibrational quantum of a proton in a molecule, but large in respect to its rotational quantum, this neutron may cause a rotation of the molecule arround one of its axes of inertia. The scattering cross-section per proton in this case is:

(1) $$\sigma = \sigma_\infty (\mu_1 \mu_2 \mu_3 \mu)^{1/2} (T_0 + T_1 + \ldots)$$

where $\sigma_\infty = 4\sigma_H (\sigma_H = 20 \cdot 10^{-24}\,cm^2$ is the cross-section for the scattering of slow neutrons by free protons); $T_0, T_1, \ldots$ are terms depending on the energy of neutrons and their Maxwellian velocity distribution and the temperature of the scattering gas; $\mu = \frac{1}{3}(\mu_1 + \mu_2 + \mu_3)$ and $\mu_1, \mu_2, \mu_3$ are the characteristic values of a tensor constructed in the following manner:

We define the so-called "mass tensor" of a molecule ($M$) by:

$$(M^{-1})_{ii} = \left( \frac{r^2_j}{I_k} + \frac{r_k^2}{I_j} + \frac{1}{M_0} \right); \quad (M^{-1})_{ij} = -\frac{r_i r_j}{I_k}$$

where $i, j, k = 1, 2, 3$; $r_1, r_2, r_3$ are the coordinates of the proton under consideration with reference to the principal axes of inertia; $I_1, I_2, I_3$ are the moments of inertia with reference to these axes; $M_0$ is the mass of the molecule. We define the tensor $n = m M^{-1}$ where $m$ is the mass of the proton. Characteristic values of this tensor are $n_1, n_2, n_3$. Now we define $\mu_1, \mu_2, \mu_3$ by:

$$\mu_1 = \frac{1}{1 + n_1}, \quad \mu_2 = \frac{1}{1 + n_2}, \quad \mu_3 = \frac{1}{1 + n_3}.$$

The Sachs and Teller theory for molecular gases may also be applied to different liquids. In this case one must replace $(T_0 + T_1 + \ldots)$

in the equation (1) by 1, so that

$$(2) \qquad \sigma = \sigma_\infty (\mu_1 \mu_2 \mu_3 \mu)^{1/2}.$$

This may be experimentally verified in the case of the following liquids: $H_2$, $H_2O$, $H_2SO_4$, $CH_3I$ (Table I).

TABLE I

| Liquid | Cross-section per molecule, as calculated according to the Sachs and Teller theory | Cross-section per molecule, obtained experimentally | Author |
|--------|-----|-----|--------|
| $H_2$ | $48{\cdot}6 \cdot 10^{-24}\,\mathrm{cm}^2$ | $48 \quad \cdot 10^{-24}\,\mathrm{cm}^2$ | Carrol 1941 (2) |
| $H_2O$ | $78{\cdot}5 \cdot 10^{-24}\,\mathrm{cm}^2$ | $85{\cdot}5 \cdot 10^{-24}\,\mathrm{cm}^2$ $81{\cdot}9 \cdot 10^{-24}\,\mathrm{cm}^2$ | Rossel 1947 (3) Janik 1951 (4) |
| $H_2SO_4$ | $119{\cdot}1 \cdot 10^{-24}\,\mathrm{cm}^2$ | $115 \quad \cdot 10^{-24}\,\mathrm{cm}^2$ | Janik 1952 (4) |
| $CH_3I$ | $195 \quad \cdot 10^{-24}\,\mathrm{cm}^2$ | $195 \quad \cdot 10^{-24}\,\mathrm{cm}^2$ | Janik 1952 (4) |

In the present note the molecular structure of methyl alcohol is investigated by the scattering of thermal neutrons on $CH_3OH$ molecules. The general structure of the $CH_3OH$ molecule is shown in Fig. 1. This structure is well known from chemical and spectroscopic data. It is possible to suppose that the hydrogen atom of the hydroxyl group rotates freely around the CO axis. But if this is true, this hydrogen atom will encounter a potential distribution with three identical maxima. If the potential barriers are sufficiently high, no free rotation will occur, but only a torsional oscillation (so-called hindered rotation) with a torsional frequency. Burkhard and Dennison [5] in their microwave spectroscopical experiments obtained the frequency $250\,\mathrm{cm}^{-1}$ and interpreted it as the torsional frequency of this hindered rotation.

The measurements of the absorption coefficient for the scattering of thermal neutrons may decide this detail of the molecular structure of methyl alcohol.

The cross-sections for the scattering of thermal neutrons on the $CH_3I$ and $CH_3OH$ molecules, calculated according to the Sachs and Teller theory assuming free rotation of the hydroxyl group in methyl alcohol, are:

$$\sigma_{CH_3I} \; = 195 \cdot 10^{-24}\,\mathrm{cm}^2$$

and

$$\sigma_{CH_3OH} = 231 \cdot 10^{-24}\,\mathrm{cm}^2.$$

The scattering cross-sections for thermal neutrons in these two liquids were experimentally determined.

The apparatus consisted of a source of photoneutrons (200 mg Ra surrounded by berylium powder) slowed down by a 6 cm layer of paraffin wax, and a detector of thermal neutrons (a boron lined ionisation chamber).

The results obtained for $CH_3I$ and $CH_3OH$ are:

$$\sigma_{CH_3I} = (195 \pm 10) \cdot 10^{-24} \, cm^2$$
$$\sigma_{CH_3OH} = (180 \pm 7) \cdot 10^{-24} \, cm^2.$$

The value obtained for $CH_3I$ is in agreement with the theory of Sachs and Teller and furnishes a new argument for the applicability of this theory to liquids. The value obtained for methyl alcohol, however, is considerably lower than that calculated on the assumption of free rotation of the hydrogen atom of the hydroxyl group around the CO axis.

It is quite natural to regard the relative torsional oscillation of the OH and $CH_3$ groups as the cause of this discrepancy. This torsional oscillation suggests that all four hydrogen atoms in methyl alcohol must be regarded as harmonical anisotropic oscillators with $\nu = 250 \, cm^{-1}$. The theory of the scattering of slow neutrons by harmonical isotropic and anisotropic oscillators was formulated by Bethe [6]. In our case, we cannot apply his equation directly on account of the possibility of the rotation of the whole molecule. At any rate it is evident that



Fig. 1. Model of the $CH_3OH$ molecule

the oscillation would cause a decrease in the theoretically evaluated scattering cross-section obtained by considering the rotational effect only.

Hence the experimentally obtained value for methyl alcohol can be accepted only in the case of the torsional oscillation of the hydrogen atom of the hydroxyl group, in qualitative agreement with the results of the microwave experiments.

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# On the Deviation from the Quadratic Dependence on the Atomic Number of the Cross-sections for Pair Production

by

## A. Z. HRYNKIEWICZ

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Measurements were performed in order to obtain the ratio of the cross-section for the production of electron pairs in Al, Cu and Ag by gamma rays of ThC'', to that in Pb. The results of these measurements were compared with values calculated from the theories of Bethe and Heitler [3], and Jaeger and Hulme [8].

According to the theory of Bethe and Heitler (1934), in which the Born approximation was employed, the cross-section for pair production is proportional to $Z^2$. According to the theory of Jaeger and Hulme (1936) the dependence on $Z$ of the cross-section for pair production is expressed by the formula

$$\sigma = a(Z/137)^2 + b(Z/137)^4$$

in which the constants $a$ and $b$, for $h\nu = 5\cdot 2$ mc$^2$ (2·62 MeV) calculated for lead, amount to

$$a = 6\cdot 95 \text{ barns}, \quad b = 4\cdot 62 \text{ barns}.$$

Some deviations from the quadratic dependence on $Z$ for light elements were obtained by Benedetti (1935, 1936) and Bocciarelli (1937); they were explained by Franchetti (1938) as being due to the background of Compton electrons. Measurements of the absorption of gamma rays of large energies (Adams (1948) [1] and Lawson (1949) [9]) in various materials in which the production of electron pairs is the main cause of absorption, proved inconsistent with theoretical calculations: for heavy elements the cross-sections were too small, for light ones too large. Recently Hahn, Baldinger and Huber [6] obtained experimentally, for elements heavier than Fe, some deviations from the quadratic dependence on $Z$ consistent with Jaeger's and Hulme's theory.

The apparatus used in the present work was, except for some slight modifications, similar to that employed before (Hrynkiewicz, 1950 [7]).

A collimated beam of gamma rays of ThC″, filtered by 25 mm of lead, was directed on the metal foil in which the electron pairs were produced. The foils were set in a light aluminium frame in order to diminish the background due to the external layers of the lead block in which the collimating channel was bored. Two G.-M. counters for beta rays with mica windows (5 mg/cm²), connected in coincidence, were placed at a distance of about 5 cm from the foil.

Besides proper coincidences caused by pair electrons produced in the foil, the apparatus could also register undesirable coincidences. The main source of possible errors arises from »Compton coincidences«, caused by a Compton electron entering one counter, and a scattered gamma photon producing an impulse in the second counter. The Compton electron may originate in the foil, in the frame in which the foil is set, or in the layer of air between the foil and the counters. Errors due to the last two sources are eliminated by subtracting the background. To eliminate the foil as a source of numerous Compton coincidences it is necessary to set the counters at the proper angle. It can easily be calculated for gamma rays of energy 2·62 MeV if we set both counters symmetrically in such a way that their effective volumes lie totally inside or outside a cone whose angle at the vertex is equal to 60⁰, Compton coincidences will not be registered. In my measurements an external setting was employed because the setting of the counters inside the cone was not convenient, owing to a large background of gamma rays.

The ratios of the number of coincidences for aluminium, copper and silver foils to the number of coincidences for lead foil were extrapolated to zero thickness in order to eliminate possible errors arising from the finite thickness of the foils. This was necessary in view of the differences of absorption in a foil of produced electrons for the same surface density of various materials and the scattering of Compton electrons from a 60⁰ cone. The extrapolation to zero thickness eliminates the error caused by these effects since they are proportional to the square of the thickness of the foil, while the number of pairs produced in the foil is directly proportional to the thickness.

The measurements consisted in registering the numbers of coincidences $N$ for Al, Cu, Ag and Pb foils of various surface densities $s$. The ratios of coincidences $N/N_{Pb}$; as a functions of $s$, were then evaluated. These values were graphically extrapolated to zero thickness. The values of $N/N_{Pb}$ obtained in such a way, as well as the theoretical ones calculated from Bethe and Heitler's, and Jaeger and Hulme's theories, are given in Table I.

The ratios of cross-sections $\sigma/\sigma_{Pb}$, calculated from experimental values of $N_{Pb}/N$, are represented in Table II. The theoretically calculated ratios are also given in this table.

TABLE I

| Element | Z | A | theoretical $N_{Pb}/N$ | | experimental |
|---------|---|---|------|------|--------------|
| | | | H.-B. | J.-H. | |
| Al | 13 | 27·0 | 5·2 | 6·5 | 3·7 ± 0·4 |
| Cu | 29 | 63·6 | 2·4 | 2·9 | 2·55 ± 0·2 |
| Ag | 47 | 107·9 | 1·6 | 1·8 | 1·7 ± 0·1 |
| Pb | 82 | 207·2 | 1·0 | 1·0 | 1·0 |

TABLE II

| Element | theoretical $\sigma/\sigma_{Pb}$ | | experimental |
|---------|------|------|--------------|
| | H.-B. | J.-H. | |
| Al | 0·025 | 0·020 | 0·035 ± 0·003 |
| Cu | 0·125 | 0·104 | 0·121 ± 0·009 |
| Ag | 0·328 | 0·286 | 0·306 ± 0·018 |
| Pb | 1·0 | 1·0 | 1·0 |

The results reported in the present note may be interpreted in such a way that the dependence of the cross-section on $Z$ is weaker than a quadratic one, which is inconsistent with the theory of Jaeger and Hulme. This conclusion would, however, be contradictory to the results obtained by Hahn et al. confirming this theory for elements heavier than Fe. Another possible explanation would be to assume that inconsistences with the theory take place in the case of lighter elements.

The author wishes to express his gratitude to Professor H. Niewodniczański for the interest he has shown in this work, and for many valuable discussions.

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# Determination of the Relative Intensities in the Triplet $4\,d^3D - 4\,p^3P^0$ in Zn I Spectrum

by

## M. D. KUNISZ •

The purpose of this work was to determine the ratios of the intensities of the spectral lines in the composed triplet $4d^3D - 4p^3P^0$ of the arc spectrum in zinc. In the experimental arrangement used, the ZnI spectral lines which were investigated appear on a continuous background of non uniform intensity. This background causes great difficulty when normal photographic methods of spectrophotometry are applied. A practical method of graphical elimination of this continuous background was elaborated.

1. Taking the light intensity of the wave length $\lambda$ as $J$ and the corresponding intensity transmitted through step $i$ of a step filter as $I_i$, we have:

$$I_i = J \cdot p_i$$

where $p_i$ is the transparency of the given segment of the filter, expressed as a fraction of 1.

Using the microphotogram of a spectrum photographed through the step filter, we may draw curves representing the relation between the plate's blackening and the intensity of the transmitted light. Let us draw two curves: the first, $S_{l+b}(I)$, representing the plate's blackening as a function of the light intensity where the blackening for the line is determined together with the continuous background, and the second, $S_b(I)$, giving the relation between the blackening of the plate and the light intensity for the continuous background where the line is located, this background being graphically determined from the microphotometer curve. These curves may serve us for obtaining a proper blackening curve for this spectral line. Further considerations refer to the drawing representing the curves of the relation between the plate's blackening and the light intensity (Fig. 1).

Let us denote by the index 1 the ordinate corresponding to the transparency $p_1$ for which the blackening of the background is $S_b^1$ and the blackening of the spectral line together with the background is $S_{l+b}^1$. Sim-

ilarly, 2 denotes the ordinate for which the blackening of the background alone $S_b^2$ is equal to that corresponding to the ordinate 1 of the spectral line together with the background, so:

$$S_b^2 = S_{l+b}^1.$$

The latter ordinate corresponds to the transparency $p_2$.

Since for the same wave length the same plate and the same time of exposure equal blackenings correspond to equal light intensities, we may write:

(1) $$I_b^2 = I_{l+b}^1$$

or $$J_b \cdot p_2 = J_{l+b} \cdot p_1 = (J_l + J_b) \cdot p_1$$

Hence

$$J_b (p_2 - p_1) = J_l \cdot p_1$$



Fig. 1

Let us denote by $p_3 = p_2 - p_1$ the ordinate for which the transparency is equal to the difference of the transparencies $p_2$ and $p_1$. Then we may write (1) as follows:

2) $$J_b \cdot p_3 = J_l \cdot p_1$$

From (2) we conclude that if the line appeared without the background, it would have the same intensity for the transparency $p_1$ of the light filter as the background for the transparency $p_3$ and so it would cause a blackening of the plate equal to the blackening of the background for the transparency $p_3$.

In this way, using the curves $S_{l+b}(I)$ and $S_b(I)$, we may find for different values of transparency $p$ the values of the blackenings of the spectral line when appearing without the background. Using these values we may draw for our line the curve $S_l(I)$ representing the dependence of the blackening of the photographic plate upon the light intensity.

After drawing similar curves for all investigated lines we may find the ratios of their intensities by applying the usual Dorgelo method.

2. In our experiment a carbon arc was used as the light source, and in this arc one of the carbon electrodes was filled with a mixture of pulverized $ZnSO_4$ and carbon.

The spectrum was photographed through a rotating linear six step sector using a large C. Zeiss-Jena quartz spectrograph with a dispersion of $18{\cdot}4 - 19{\cdot}0$ Å. U./mm in the investigated spectral region. "Omega" photographic plates made by "Film Polski" were used.

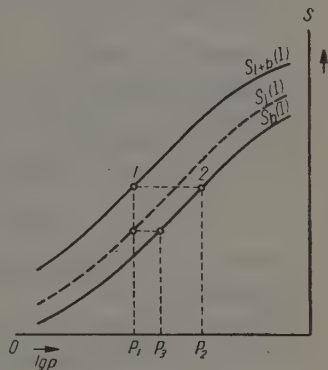The blackening of the plates was measured by means of a C. Zeiss-Jena photoelectric microphotometer.

Some preliminary investigations proved, with a mean probable error of $2\%$, that the blackening of the photographic plates is independent on the wavelength in the spectral region under consideration.

For the lines:

$\lambda$ 3345 Å. U. $[(4d^3D_3 - 4p^3P_2^0) + (4d^3D_2 - 4p^3P_2^0) + (4d^3D_1 - 4p^3P_2^0)];$
$\lambda$ 3303 Å. U. $[(4d^3D_2 - 4p^3P_1^0) + (4d^3D_1 - 4p^3P_1^0)];$
$\lambda$ 3282 Å. U. $(4d^3D_1 - 4p^3P_2^0),$

the following relative intensities were obtained:

$$J_{3345} : J_{3303} : J_{3282} = 100 : (60 \pm 1) : (22 \pm 2)$$

Allowing for experimental error, these values are in good agreement with the summation rule.

I wish to express my gratitude to Professor H. Niewodniczański for many interesting and helpful disscussions in the course of these investigations.

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# Extinction thermique de fluorescence des solutions de biacène

par

## K. ROSIŃSKI

*Présenté par S. PIEŃKOWSKI à la séance du 22 Septembre 1952*

P r é f a c e. En étudiant l'extinction thermique de fluorescence de rubrène dans divers solvants, E. J. Bowen [1] suppose qu'elle est causée par une activation thermique à laquelle est soumise une molécule fluorescente. L'énergie d'activation étant de $\sim 7{\cdot}0 \dfrac{\text{kcal}}{\text{mol}}$ caractèrise en principe la structure de cette molécule. Les travaux des physiciens soviétiques montrent que l'énergie d'activation dépend d'une manière essentielle de la nature du solvant [2].

C'est l'étude de l'extinction thermique de la fluorescence des divers solutions de biacène, qui fait l'objet du présent travail. Dans la note présente nous résumons des résultats obtenus pour une solution de biacène dans le silicon.

A p p a r e i l l a g e. La solution de biacénaphtylidène ($C_{24}H_{16}$) dans le silicon $DC$ 703 était d'une concentration de l'ordre de $10^{-5}$ g/g.

Pour des mesures d'inténsité de la fluorescence nous nous sommes servis de la méthode de photométrie photographique, employant un dipositif expérimental typique.

La solution examinée, contenue dans une cuvette évacuée, se trouvait dans un thermostat pourvu d'un réglage électrique de la température. La constance de la source lumineuse excitant la fluorescence (la lumière de l'arc à mercure filtrée par un verre de Wood) était contrôlée à l'aide d'une cellule photoélectrique. Le spectrographe avait une dispersion de $18 \dfrac{\text{Å}}{\text{mm}}$ (à la région de 4356 Å). La largeur utilisée de la fente était de 0·30 à 0·40 mm. La concentration de la solution était choisie de telle sorte que la réabsorption de la fluorescence par la solution fut réduite au minimum. Une échelle transparente, servant pour les mesures photométriques, était posée en intermédiaire devant la fente du spectrographe. Cette fente était illuminée d'une manière tout à fait uniforme.

R é s u l t a t s. Les résultats ainsi obtenus sont représentés sous la forme d'un diagramme (Fig. 1), donnant le rapport entre l'intensité $J$ de la fluo-

rescence et la température $t$. L'intensité $J$ est mesurée par rapport à l'intensité $J_0$ correspondant à la température de 20° C.

Ce diagramme n'indique aucun rapport simple entre $J$ et $t$. C'est pourquoi, pour expliquer la forme trouvée de cette courbe, nous introduisons l'hypothèse suivante concernant le mode de désactivation de la molécule éxcitée.

Supposons que cette désactivation résulte en général d'une conversion interne d'énergie de l'excitation électronique. L'examen des courbes de potentiel $N$ et $E$ correspondant aux états: normal et éxcité de la molécule, permet de préciser cette idée. Des courbes correspondent à un seul degré de liberté de vibration. Notons que dans le cas d'une molécule organique
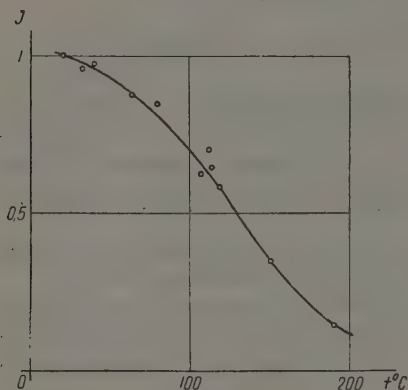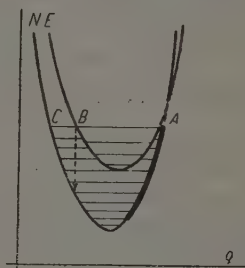


Fig. 1



Fig. 2

complexe, hautement symétrique, on peut examiner un seul degré de liberté de vibration, le couplage avec d'autres étant très faible, et qu'ensuite ce sont des vibrations de torsion qui conduisent à la conversion interne particulièrement effective.

Une molécule se trouvant au niveau $AB$ (Fig. 2) peut passer de l'état éxcité à l'état normal électronique, avec l'émission de la lumière (ligne interrompue commençant à $B$), mais également au niveau $AC$ de vibration, plus élevé que l'état normal, d'où après une dissipation de l'énergie de vibration en chaleur — à un niveau normal de vibration (ligne épaisse). Ce dernier passage s'effectue sans émission de lumière et constitue ainsi la conversion interne.

Quand la température croît, les molécules excitées passent aux niveaux plus élevés de vibration ($AB$), comme résultat de la répartition d'énergie thermique dans la solution. Ainsi le nombre des molécules se trouvant au niveau $AB$ croît, ce qui amène une augmentation de la possibilité de la conversion interne. C'est en cela que réside la raison de l'extinction thermique.

Remarquons que dans le cas du biacène il y a deux configurations planes stabiles dont les schémas sont représentés sur la Fig. 3. Ces sché-



*Configuration α*
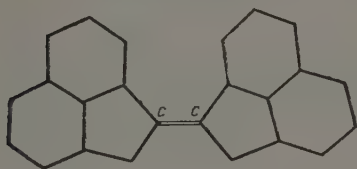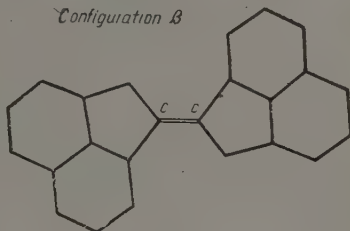
Fig. 3 a
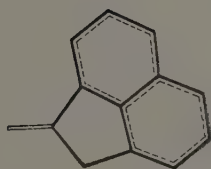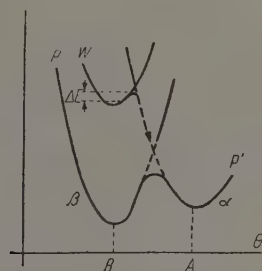
*Configuration β*

Fig. 3 b



Fig. 3 c



Fig. 4

mas de structure (donnés jusqu'ici sous une forme trop simplifiée) sont donnés ici d'après l'introduction d'une correction des angles de valence ainsi que des distances atomiques. Supposons en plus que la rotation plane des groupements moléculaires autour de la ligne de liaison $C = C$ peut être représentée par une courbe de potentiel montrée sur la Fig. 4, où les minimums $A$ et $B$ de potentiel correspondent aux configurations stabiles $\alpha$ et $\beta$. La courbe de potentiel $W$ de l'état éxcité de la forme $\beta$ coupe celle de l'état normal de la forme $\alpha$ en un point qui se trouve sur une hauteur $\Delta E$, au dessus de l'état normal de vibration à l'état électronique éxcité.
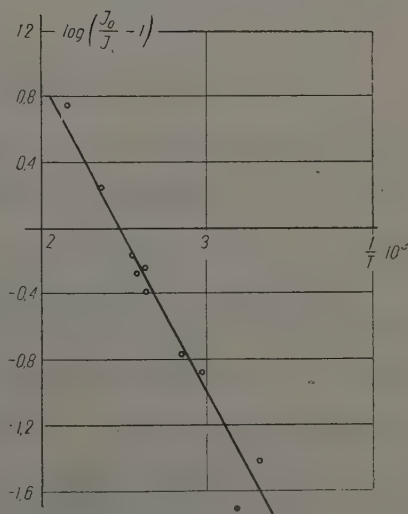


Fig. 5

Or, la transition du niveau normal de vibration de la forme $\beta$ se trouvant dans l'état électronique éxcité, à un niveau de vibration plus élevé de la forme $\alpha$ à l'état électronique normal (courbe $P'$) peut être considérée comme analogue à un passage par une barrière du potentiel d'une hauteur $\Delta E$. Notons que, selon les suppositions ci-dessus, cette transition ($W \rightarrow P'$) amène ainsi l'extinction de la fluorescence. C'est donc l'énergie d'agitation thermique qui peut servir comme source d'énergie de cette transition.

Désignons maintenant par $d$ la probabilité d'extinction de la fluorescence, c'est-à-dire de la transition $W \rightarrow P'$ par une barrière de potentiel $\Delta E$. Evidemment cette probabilité est proportionnelle au nombre des molécules douées d'une énergie de vibration $\Delta E$, ce nombre étant proportionnel, selon la statistique de Maxwell-Boltzmann, au facteur:

$$e^{-\frac{\Delta E}{kT}}$$

ainsi

$$d = Ae^{-\frac{\Delta E}{kT}};$$

on vérifie facilement les relations suivantes:

$$\frac{J_0}{J} = \frac{\varrho_0}{\varrho} = \frac{d+f}{f} = 1 + \frac{d}{f},$$

où $J_0, J, \varrho_0, \varrho$ désignent respectivement l'intensité et le rendement de la fluorescence sans et avec extinction, $f$ étant la probabilité de transition avec l'émission de la lumière.

Nous avons enfin:

$$\frac{J_0}{J} - 1 = Ce^{-\frac{\Delta E}{kT}}, \text{ où } C = \frac{A}{f} \text{ et } \ln\left(\frac{J_0}{J} - 1\right) = \ln C - \frac{\Delta E}{k} \cdot \frac{1}{T};$$

nous voyons que cette formule représente une relation linéaire entre $\ln\left(\frac{J_0}{J} - 1\right)$ et $\frac{1}{T}$. Représentons maintenant les résultats de nos mesures dans les coordonnées $\left[\log\left(\frac{J_0}{J} - 1\right), \frac{1}{T}\right]$.

Nous recevons ainsi une ligne droite (Fig. 5), ce qui est d'accord avec l'hypothèse qui a été proposée ci-dessus. La valeur de l'énergie d'activation donnée par la courbe Fig. 5, est égale à $8{,}5 \frac{\text{k cal}}{\text{mol}}$. Remarquons que l'énergie thermique à la température de $20^0$C est de l'ordre de $0{,}6 \frac{\text{k cal}}{\text{mol}}$. Ainsi, nous voyons que la conversion interne de l'énergie d'excitation électronique est liée à la valeur de l'énergie thermique de la solution.

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# On the Application of the Nuclear Emulsion Method to the Determination of the Absorption Coefficients of Slow Neutrons

by

## M. WIELOWIEJSKA

*Communicated by H. NIEWODNICZAŃSKI at the meeting of October 20, 1952*

A statistical photographic method of the measurement of the flux of thermal neutrons was elaborated. This method was applied to the determination of the cross-sections of the aluminium and lead atoms for the absorption of thermal neutrons.

A source of photoneutrons from the reaction ${}^{9}_{4}\mathrm{Be}(\gamma, n)2{}^{4}_{2}\mathrm{He}$ was used. It consisted of about 13 mg of radium (in equilibrium with its products) surrounded by about 1ˑ3 g of beryllium powder in a cylindrical box of which both the diameter and height were about 6 cm. To slow down the neutrons (with initial energies about 0ˑ2 and 0ˑ6 MeV) the source was placed in a hollow cylinder of paraffin wax with walls 6 cm thick. After traversing this layer of paraffin wax the neutrons may be regarded as »thermal« ones with a mean kinetic energy of about 0ˑ025 MeV corresponding to room temperature.

In a suitable experimental arrangement the beam of neutrons filtered by a layer of lead passed through the different absorbers under investigation to a nuclear emulsion plate placed perpendicularly to the direction of the beam of neutrons. A rather thick filter of lead was necessary in order to diminish the intensity of the strong background of gamma radiation accompanying the photoneutrons. The most suitable thickness of the lead filter was found experimentally to be about 5 cm. It weakened the flux of thermal neutrons to about $1/4$ of that obtained without the filter but at the same time diminished the background, produced by the $\gamma$-radiation in the emulsion of the plate, sufficiently to make it possible to measure and count the tracks of ${}^{3}\mathrm{H}$ and ${}^{4}\mathrm{He}$ nuclei from the reaction ${}^{6}\mathrm{Li}(n, \alpha){}^{3}\mathrm{H}$.

Ilford C2, $100\,\mu$, lithium loaded nuclear emulsion plates were used. A thermical method of developing was used. Owing to the great weakness of the source of neutrons and the relatively strong $\gamma$-ray background, the

optimum time of exposure amounting to 96 hours for all final measurements was adopted, the geometry of the experiments being maintained constant for all exposures.

The plates were elaborated using a magnification of $588 \times$, found to be the most convenient for the measurements of the tracks of $^3$H and $^4$He particles, of the common length of $42\,\mu$, as determined also by Titterton (1949) [3] and Locqueneux (1950) [2].

Since the lengths of all tracks are equal and their distribution isotropic, they are generally more or less inclined to the plane of the field of vision in the microscope. Both the length of the projection of the tracks on the plane of vision, and their depth, were measured. When determining the depth, the contraction of the dried emulsion for the Ilford C 2 plates was taken as $2\cdot16$ — fold, according to Vigneron (1949) [4].

A statistical method was developed for determining the relative intensity of the flux of thermal neutrons, based on the measurements of the density of tracks of which the length of the component parallel to the plane of vision fell between 12 and $42\,\mu$. The validity of this method was checked in several cases, using different methods of statistical treatment of the experimental results.

Using this method several experiments were performed in order to determine the mean cross-sections of the aluminium and lead nuclei for the total absorption (i. e. for capture and scattering) of thermal neutrons.

In Figs 1 and 2 the logarithms of the relative numbers of neutrons which traversed the absorbers of lead and aluminium respectively, and
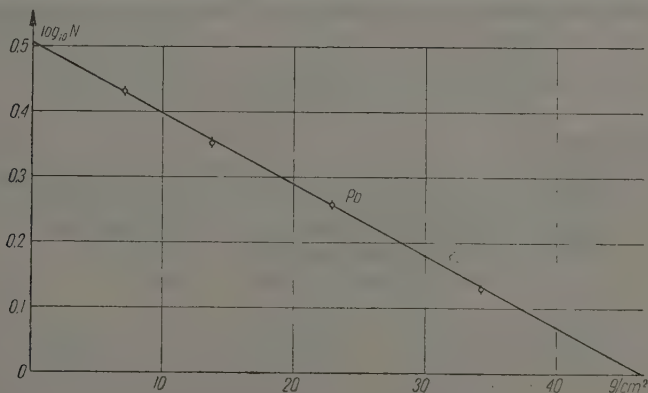


Fig. 1

reached the photographic plate, are plotted against the thickness of the absorber given in g/cm². A well defined linear dependence allows us to determine the total absorption coefficients for thermal neutrons for both

lead and aluminium. The figures obtained are as follows:

$$\mu_{Al} = (0{\cdot}09851 \pm 4\%)\,\mathrm{cm}^{-1}$$
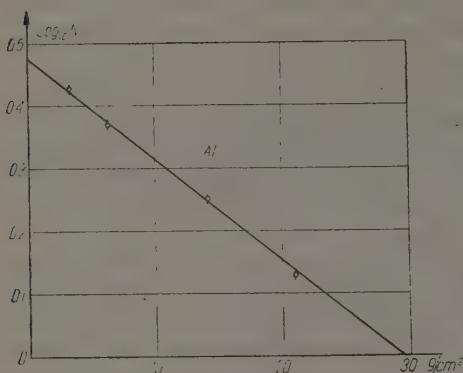$$\mu_{Pb} = (0{\cdot}2847 \pm 4\%)\,\mathrm{cm}^{-1}.$$



Fig. 2

According to these numerical values the mean absorption cross-sections of the Pb and Al nuclei for the total absorption of thermal neutrons were calculated. These are as follows:

$$\sigma_{Al} = (1{\cdot}64 \pm 4\%)\ \mathrm{barns}$$
$$\sigma_{Pb} = (8{\cdot}63 \pm 4\%)\quad,,\quad .$$

These figures are in good agreement with the results obtained by other methods (see [1].)

The absolute sensitivity of this photographic method of measuring the flux of thermal neutrons, when Ilford C2 $100\,\mu$ lithium loaded plates are used, is shown by the smallest surface density of about $10^6$ neutrons per cm² which may be determined with a satisfactory small statistical error.

The author wishes to express his gratitude to Professor H. Niewodniczański who suggested this problem, and for his many helpful discussions during its execution.

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# Classification of Negative Azeotropes XIV

by
## W. ŚWIĘTOSŁAWSKI

*Communicated at the meeting of September 22, 1952*

1. N e g a t i v e   A z e o t r o p e s. We call negative binary azeotrope a mixture of two liquids which form an isotherm with a minimum vapour pressure. The number of known negative azeotropes is not as large as that of positive ones. In spite of this they play an important role in the understanding of the phenomena which take place when different kinds of liquid mixtures are submitted to a fractional distillation. Their significance increases with the discovery of a large number of ternary positive-negative azeotropes which constitute the subject of the next paper in this series In order to give an adequate explanation of the phenomena which take place when a negative binary azeotrope forms with a third component a ternary positive-negative one, the classification of binary negative azeotropes seems to be of considerable importance.

2. T h r e e   G r o u p s   o f   N e g a t i v e   A z e o t r o p e s. It is generally accepted that a minimum vapour pressure appears if the attractive forces $a_{1\cdot 1}$ and $a_{2\cdot 2}$ acting between molecules of each of the component 1 and 2 are weaker than those $a_{1\cdot 2}$ acting between two different molecules:

$$a_{1\cdot 1} < a_{1\cdot 2} > a_{2\cdot 2}.$$

In spite of this, a relatively large number of negative azeotropes are known in which, besides van der Waals' forces, chemical or electrochemical ones are responsible for the formation of minimum vapour pressures and maximum boiling points. Taking this into consideration the following classification of binary negative azeotropes composed of components other than water may be accepted. According to this classification the negative azeotropes should be divided into three groups: to the first group belong binary negative azeotropes in which the inequality between van der Waals' forces:

$$a_{1\cdot 1} < a_{1\cdot 2} > a_{2\cdot 2}$$

is responsible for the appearance of a minimum vapour pressure. A relatively large number of negative azeotropes of this group is known, e. g. chloroform and acetone, pyridine and some of the alcohols, etc.

To the second group belong all dehydrated mixtures composed of a weak acid and a weak base.

As yet, only a relatively small number of these mixtures has been carefully examined. Among them, azeotropes formed by acetic acid or phenol and different aromatic bases, especially pyridine and its homologues, are listed in two Horsley's, and in Lecat's, tables.

The third group comprises mixtures of a weak base with a strong acid or a weak acid with a strong base.

Up to now, the properties of several mixtures belonging to the third group have been examined but not as azeotropes. They have been treated rather as salts. For instance pyridine and its homologues, as well as some aromatic amines, form volatile hydrochlorides which may be submitted to fractional distillation. In solutions and in the solid phase they behave as salts formed by equivalent amounts of the two components. For this reason they have not been listed in the tables as negative azeotropes. The phenomena are quite different if the hydrochlorides mentioned above are submitted to fractional distillation. Under constant pressure they boil and distill at constant temperatures but, in spite of this, their distillation products do not correspond to the composition of salts. They contain more hydrogen chloride than salts do. That is why they should be treated rather as binary negative azeotropes. Because of the chemical forces involved, the increases in the boiling points of the corresponding negative azeotropes are very high compared with the increases in the boiling points of two other groups of these azeotropes. Usually their boiling points are more than one hundred degrees higher than the corresponding bases. For this reason they must be considered as interesting subjects for examination as azeotropic agents.

We hope soon to be able to present the results of some experiments with these azeotropic agents.

In the note which follows, representatives of all three groups of binary negative azeotropes are examined with respect to the formation of so-called saddle or ternary positive-negative azeotropes.

### SUMMARY

Negative binary azeotropes composed of components other than water have been divided into three groups. This classification is based on different types of intermolecular forces responsible for the appearance of the minimum vapour pressures and the maximum boiling temperature. To the first group belong azeotropes in which the molecules of the two components attract each other with larger van der Waals' forces than those with which the molecules of one component are attracted. To the second group belong dehydrated mixtures of weak bases and weak acids. The third group is composed of dehydrated mixtures of weak bases and strong acids and vice versa.

REFERENCES

The references to a series of papers on azeotropy already published (I—VIII) or in press (IX—XIII) are listed below:

In Polish: I—V — Roczniki Chem. **25** (1951), 86—111. VI—VIII ibid. **25** (1952), 351—402.

In English: I—V — Bull. Acad. Sci. Polonaise 1950 A, 9—33, VI—VIII ibid. 1951 A, 87—108.

# On Ternary Positive-Negative Azeotropes XV

by

## W. ŚWIĘTOSŁAWSKI

*Communicated at the meeting of September 22, 1952*

1. Introductory Remarks. Ternary positive-negative, or saddle, azeotropes are systems composed of two components of a binary negative azeotrope, and a positive azeotropic agent which either may or may not form binary positive azeotropes with each of the components of the negative azeotrope. The classification of these ternary saddle azeotropes should be based on that suggested in the previous note (XIV) for the binary negative azeotropes. For this reason the ternary azeotropes under consideration may be formed by the components of any type of the negative ones.

2. Investigations on ternary saddle azeotropes. Up to the present only one ternary positive-negative azeotrope has been described ([1] and [2]). This was composed of chloroform, acetone and methanol. No general discussion with respect to the formation of similar other azeotropes has been given.



Fig. 1. Scheme representing a ternary positive-negative azeotrope. $A, P$ and $H$ represent a weak acid, a weak base and a hydrocarbon. $HC$ is the main or median line. $Az$ is the point representing the composition of the ternary positive-negative azeotrope $[(-)A, P(+)H]$

In September 1951, at the suggestion of the present author, a group of Polish physico-chemists: Mrs. H. Majewska, K. Zięborak, Mrs. M. Zięborak, T. Bogucki and a number of others, started to carry out experiments with a series of ternary positive-negative azeotropes belonging to the second group, according to the classification given in the preceding note.

The subjects of our investigations form together a system of ternary positive-negative azeotropes with a common weak base $(P)$ and weak acid $(A)$ as components of a binary negative azeotrope. The third component $(H)$ is as a rule anyone of the hydrocarbons.
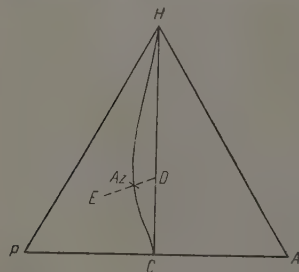
3. Symbols used. In previous notes of the same series [3] we used the symbols $(A, H_i)$, $(A, B, H_i)$ and $(A, B, C, H_i)$ to designate binary,

ternary and quaternary positive azeotropes formed by series *(H)* of homo-
logues, their isomers or other chemically related substances with agent *A, A*
and *B*, or *A, B* and *C*, respectively. In this paper, which deals with binary
negative azeotropes or ternary and quaternary positive-negative ones, we
use the following symbols:

|  |  |
|---|---|
| TYPE OF AZEOTROPE | SYMBOLS |
| Binary negative | $[(—)A, P]$ |
| Ternary positive-negative | $[(—)A, P(+)H]$ |
| Quaternary positive-negative | $[(—)A, P(+)H, B]$ |

In spite of the fact that quaternary positive-
negative azeotropes have not as yet been dis-
covered, there is no doubt at all that they
do exist. As the components we have, up to
the present, used aceticacid, phenol and cres-
ols as weak acids; and pyridine, isomeric pic-
olines and lutidines, as well as some of the
aromatic amines, as weak bases. The third
component was one of the aliphatic or aromatic
hydrocarbons.

4. Composition of Ternary Pos-
itive-Negative Azeotropes. Let us
suppose that azeotrope $[(—)A, P(+)H]$ is the
subject of our investigation. If the Gibbs
triangle of concentrations is used (Fig. 1)
then we will find, on line *AP*, point *C* re-
presenting the composition of the negative
binary azeotrope $[(—)A, P]$. Below, we will
call line *HC* the **main or median line**.

Point *Az*, representing the composition
of the ternary positive-negative, sometimes
called saddle, azeotrope, may be found either
on main line *HC* (point *D* in fig. 1) or inside
one of the two triangles *AHC* or *PHC*. Let
us examine first two cases in which point *Az*
lies on the main line. Both of them depend
exclusively upon the boiling point of the
hydrocarbon used. In fact, if it boils so low
(or so high) that the isobars formed by it
and the negative azeotrope $[(—)A, P]$ are tan-
gent, or almost tangent, to the horizontal planes
drwan through point *H* or *C* respectively, the



Fig. 2. Tridimensional scheme
of a system of ternary positive-
negative azeotropes  $[(—)A, P$
$(+)H]$ composed of acetic acid
*(A)*, pyridine *(P)* and a series of
paraffinic and naphthenic hyd-
rocarbons $H_1, H_2 ... H_n$. *H* is
one representative of the series;
*Az* is the location of the azeot-
ropic point corresponding to
the azeotrope containing *H*
as the third component; $t_{(—)Az}$
represents the boiling point of
negative azeotrope $[(—) A, P]$;
$t_H Az—Az$ is the top-ridge line
on which all the azeotropic
points of the whole system of
azeotropes formed by *A, P* and
series $H_1, H_2 .. H_n$ lie

composition of the ternary azeotrope is identical, or practically identical
with that represented by point *H* or *C*.

5*

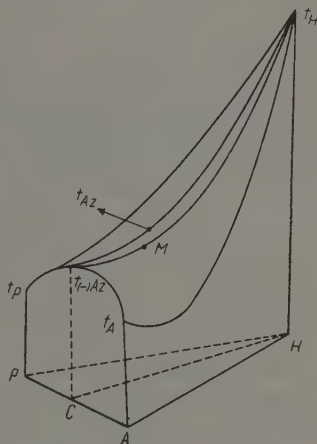There is another, more general, case in which point $Az$ representing the composition of the ternary azeotropes always lies either on line $HC$ or in close proximity to it. In this kind of azeotropes the negative partner plays the dominant role. It should belong to the third group of negative azeotropes and should contain as one of its components either a strong acid or a strong base. In this type of negative azeotrope the acting forces are so strong that when a third, neutral agent is added to those azeotropes, the molar relation $A:P$ remains practically constant and for this reason point $A_z$ lies on main line $HC$ or very close to it.
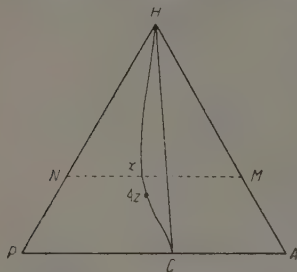


Fig. 3. Scheme showing the projection of the top line on the concentration triangle. Each point lying on the top line corresponds to the maximum boiling point $x$ of a mixture of $N$ and $M$ in the ratio $Nx:Mx$. Azeotropic point $Az$ of azeotrope $[(-)A, P(+)H]$ on the top line

In the case of negative azeotropes of the first and the second group the attractive forces acting between $A$ and $P$ are too weak for the relation $A:P$ undergo a change.

In Fig. 1 points $E, Az$ and $D$ represent the three possible locations of the point corresponding to the composition of the ternary positive-negative azeotrope. If the negative azeotrope belongs to the first group (van der Waals forces), the location of the azeotropic point is often located far from line $HC$ (for instance point $E$). In the case where a negative azeotrope is formed by a weak acid and a weak base (second group), the azeotropic point is found somewhere between $E$ and $D$ (point $Az$). As to the third group of negative azeotropes, we have already explained, why the azeotropic point lies on line $HC$ (point $D$).

5. T o p   L i n e. In Fig. 2 a tridimensional presentation of a ternary saddle azeotrope is given. In this figure, points $A$ and $P$ represent a weak acid and a weak base. Point $H$ corresponds to a parraffinic, naphthenic or aromatic hydrocarbon, which forms with $A$ and $P$ a ternary positive-negative azeotrope of type $[(-)A, P(+)H]$. Points $t_A$, $t_P$ and $t_H$ represent the normal boiling points of the components $A, H$ and $P$. The dotted line $HC$ is the main line. It is at the same time the projection of the isobar formed at $p = 1$ atmos. by component $A$ and azeotrope $[(-)A, P]$. Curve $t_{(-)Az} t_{Az} t_H$ represents the line on which the azeotropic point $t_{Az}$ lies. This line we call the top one, because each point on it corresponds to the maximum boiling point found for a mixture of $N$ and $M$, as shown in Fig. 3.

The method for determining the boiling point and the composition of azeotrope $[(-)A, P(+)H]$ based on the schemes shown in Fig. 1. 2 and 3 is described in the paper which follows.

## SUMMARY

A scheme of the formation of ternary positive-negative azeotropes has been discussed. The location of the azeotropic point of ternary azeotrope $[(-)A, P(+)H]$, in which $A$ stands for a weak acid, $P$ for a weak base and $H$ for a hydrocarbon, depends upon the nature of components $A$ and $P$ of negative azeotrope $[(-)A, P]$ formed by them. This point may lie on the main line ($HC$ shown in Fig. 1), or inside triangles $AHC$ or $HCP$. The former case may be expected when $A$ or $P$ is a strong acid or a strong base. When $A$ and $P$ are a weak acid and a weak base the point is located near median line $HC$. Finally, it is found somewhere far away from line $HC$, if between molecules of $A$ and $P$ van der Waals forces are predominant (point $E$ in Fig. 1).

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# A Method for Determining the Composition and the Boiling Point of Ternary Positive Negative Azeotropes XVI

by

## W. ŚWIĘTOSŁAWSKI

*Communicated at the meeting of September 22, 1952*

1. Peculiar Properties of Ternary Positive-Negative Azeotropes. The investigations described a few years ago by Ewell and Welch [1] have shown some peculiar properties of ternary positive-negative azeotropes. When examining some mixtures of chloroform, acetone and methanol, the authors mentioned above observed, in the course of distillation, a sudden drop of the condensation temperature. We have observed similar phenomena when operating with more complicated systems. For this reason there is some danger of obtaining faulty results in experiments conducted with a view of preparing a ternary positive-negative azeotrope by distillation. To avoid errors an ebulliometric method for determining the composition and the normal boiling point of these azeotropes has been recently used in our laboratory. In a number of experiments carried out up to the present, this method has never failed. It is based on a modification of two methods, the "triangle" and the "star" methods described in "Ebulliometric Measurements" [2] and in "Ebulliometry" [3].

2. A Method for Determining the Composition and the Boiling Point of Ternary Saddle Azeotropes. Referring to the preceding note we should recall that, with some exceptions previously disscused, the composition of the ternary saddle azeotrope is usually represented in Gibbs concentration triangle by point $Az$ lying not very far from main line $HC$ (Fig. 1) (XV).

It is located either inside triangle $AHC$ or $PHC$, and usually not far from point $M$, which lies on the main line $HC$ and corresponds to the minimum boiling point of a mixture composed of binary negative azeotrope $[(-)A, p]$. And component $H$, taken in amounts given by the relation:

$$[(-)A, P]: H = CM: MH.$$

For this reason the first step which should be undertaken is to examine the isobar formed by azeotrope $[(-)A, P]$ and component $H$. The most convenient way is to use a differential ebulliometer with standardised dimensions [2]. Usually three series of measurements should be carried out. One of these consists in adding substance $H$ to azeotrope $[(-)A, P]$ and examining the boiling and the condensation points of the mixtures obtained after each successive addition of $H$. After the "saddle" section of the tridimentional surface is reached, the changes in boiling and condensation points of the corresponding mixtures start to be very small. Usually, after a dozen of dosings the ebulliometric vessel becomes overcharged with the liquid. At this time the heating should be discontinued, half the liquid poured out of the ebulliometer, and the weight of liquid removed determined. Af-terwards, another series of dosing should be carried out, to the point at which the mixture in the ebulliometer reaches the composition of $70\%$ $H$ and $30\%$ $[(-)A, P]$. Now the ebulliometer should be cooled and the entire mix-ture poured out. In place of it pure substance $H$ should be placed in the ebulliometer. This time known amounts of $[(-)A, P]$ must be added successively to $H$ and the third set of measurements of boiling and condensation points of the mixtures thus obtained should be completed. On the basis of these data one has to interpolate the position of point $M$ cor-responding to the minimum boiling point of the isobar thus obtained. The next set of mea-



Fig 1. Determination of com-position $M$ of the mixture com-posed of binary negative azeo-trope $[(-)A, P]$ and component $H$. Point $M$ represents the com-position of the mixture charac-terised by minimum boiling point. Az is the point corresponding to the composition of ternary sad-dle azeotrope $[(-)A, P (+)H]$

surements should be carried out in the following way. We draw three horizontal lines as shown in Figs. 1 and 2, the middle one through point $M$ characterised by maximum boiling point.

We obtain in this way points 1, 2 and 3 lying on the main line and points 1', 2', 3' and 1'', 2'', 3'' lying on lines $PH$ and $HA$, respectively Now we fill the ebulliometer with the mixture given by point $M$ and we add successively small amounts of the mixture represented by point 2'. One of two possible cases will be observed: either the boiling point will decrease or it will increase. In the first case the conclusion should be drawn that the azeotropic point is located inside triangle $AHC$, in the second that it is found inside triangle $PHC$. Knowing this, we carry out three (or more) sets of measurements. First, we add to mixture 2 (point $M$) successively mixture 2' and we measure after each addition the boiling and the condens-ation points of the mixtures thus obtained. In this way we find the com-position of the mixture boiling at a minimum boiling point. In the next
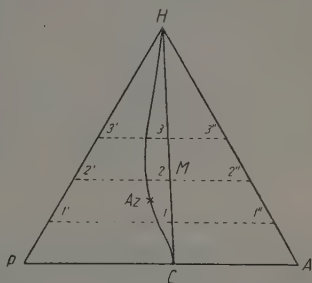
two experiments we add to mixture 1 mixture 1′, and to 3 mixture 3′. In each experiment we determine the composition of the mixture characterized by a maximum boiling point.

In Fig. 2 the results obtained in conducting such a set of measurements are given. The boiling point of the ternary positive-negative azeotrope is the lowest one interpolated according to the data collected.
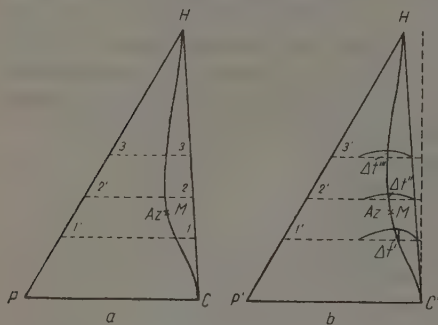


Fig. 2. Scheme showing a graphical determination of maximum boiling points on isobars obtained by mixing 1 with 1′, 2 with 2′, and 3 with 3′. Point $Az$ is interpolated as having the minimum value $\Delta t_m$ of the boiling point increases

3. S h a p e of the Saddle Section. Ternary saddle azeotropes examined up to this time by the method mentioned above have shown that the section which corresponds to the lowest part of the saddle possesses an exceedently small curvature, so that the temperature changes do not exceed $0.5°$ for large concentration changes. This is especially characteristic for azeotropes formed by acetic acid, pyridine and isomeric picolines and lutidines on the one hand, and hydrocarbons boiling in the range from $98°$ to $195°\,C$ on the other. For this reason, the exact determination of the real boiling point of the azeotrope under examination requires precise temperature measurements.

We have used up to this time differential ebulliometers with standardised dimentions, in order to examine the boiling and the condensation point of each of the mixtures examined. We think, however, that it is more reasonable to use three-stage ebuliometers [2] so as to be able to measure the boiling and the condensation points of each of the mixtures investigated. In fact, all the azeotropes thus far examined are exceedingly hydroscopic. Very small amounts of moisture cause a considerable change in the boiling, and predominantly in the condensation points of the mixtures examined. In the case of the three-stage ebulliometer the second condensation point $(t_b)$ will indicate whether some amount of water is circulating in the upper part of the ebulliometer. The first condensation point $(t_1)$ should show no presence of moisture. Difference $\Delta t_1$:

$$t_b - t_1 = \Delta t_1$$

between the boiling point and the first condensation point $\Delta t_1$ should indicate the presence of impurities accompanying substances $A$, $P$ and $H$. On the contrary, difference $(t_1 - t_2) = \Delta t_2$ should be caused by the presence of very small amount of moisture. For controlling the results obtained a mixture

must be prepared containing the percentages of $A$, $P$ and $H$ equal to those found by the method described. It should be submitted to a careful fractional distillation. The main fraction collected should boil at a constant temperature equal to that found by extrapolation as shown in Fig. 2.

## SUMMARY

1. Peculiar properties of ternary positive-negative azeotropes make it impossible to use the fractional distillation method for preparation of these azeotropes.

2. A method for determining the compositions and the boiling points of ternary saddle azeotropes has been described. It consists in finding the minimum boiling temperature $t_m$ of a mixture composed of binary negative azeotrope $[(-)A, P]$ and of the third agent $H$. Point $M$ corresponding to the projection of $t_m$ on median line $HC$ should be found. Through point $M$ and two others lying above and below the latter, parallel horizontal lines should be drawn, and isobars of mixtures of 1 with 1′, 2 with 2′, and 3 with 3′ should be examined. In this way the maximum boiling temperatures of mixtures lying on the top line may be found. By interpolation, the location of the point representing the composition of the azeotrope may be fixed. Its boiling temperature may also be interpolated.

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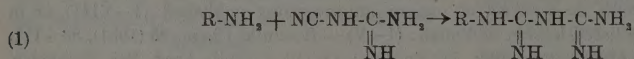
# On Reactions of Aromatic Amines with Cyanguanidine. Formation of Aryl-Derivatives of Amidine-Urea and Their Transformation into Carbanilides

by

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It is well known that aromatic amines and cyanguanidine can readily form the corresponding biguanides:

$$\text{R-NH}_2 + \text{NC-NH-}\underset{\overset{\|}{\text{NH}}}{\text{C}}\text{-NH}_2 \rightarrow \text{R-NH-}\underset{\overset{\|}{\text{NH}}}{\text{C}}\text{-NH-}\underset{\overset{\|}{\text{NH}}}{\text{C}}\text{-NH}_2$$

(1)

The reaction takes place in the presence of mineral acids, in aqueous [1] or alcoholic [2] medium, or by fusing the amine hydrochloride with cyanguanidine [3].

It has now been found that aromatic amines, when boiled with an aqueous solution of cyanguanidine in the presence of mineral acids of higher concentrations, than that used in the reaction (1), can readily yield $N_1$-amidine-$N_2$-arylurea (I):

$$\text{R}\!-\!\!\left\langle\ \ \right\rangle\!\!-\!\text{NH·CO-NH-}\underset{\overset{\|}{\text{NH}}}{\text{C}}\text{-NH}_2$$
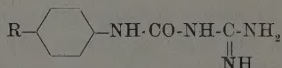
I

Up till now these compounds have been very little known, as only one of them, $N_1$-amidino-$N_2$-phenylurea (i. e. R = H), in the form of nitrate, has been described. This compound was prepared by Pellizzari [4], and recently by Junod [5], by relatively complicated methods which are different from those described in the present paper.

It has now been found that p-nitroaniline, when boiled with cyanguanidine in the presence of 22% hydrochloric acid, yields $N_1$-*amidine*-$N_2$-*(p-nitrophenyl)-urea* (III).

When p-nitroaniline was boiled with cyanguanidine in the presence of 12% hydrochloric acid, p-nitrophenylbiguanide[6]) (II) was formed. It was

also found that when (II) was boiled with 22% hydrochloric acid, the product (III) resulted.

This reaction took place with aniline, p-nitroaniline (as described above), p-aminophenol and p-aminobenzoic acid. In all cases the same facts were observed: boiling in the more concentrated acids produced substances (I), in less concentrated biguanides. The latter can be transformed into (I), if boiled in a more concentrated acid.

Table (A) gives the essentials on the formation of compounds (I). The corresponding hydrochlorides, except for the product (V), have been transformed into free bases by means of $Na_2HPO_4$ in aqueous solution.
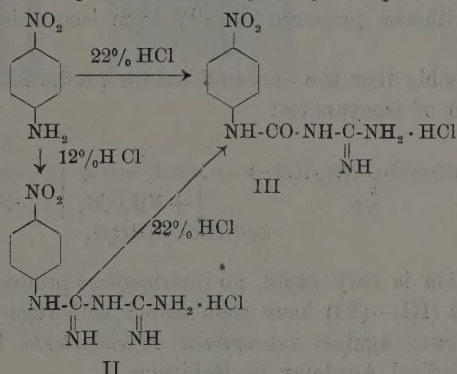


TABLE A

| Starting product | Acid used | | Number | Product formed R = (formula I) | (free bases m. p.) |
|---|---|---|---|---|---|
| aniline | HCl | ca 30% | IV | H | 166—177° |
| p-nitroaniline | HCl | ca 22% | III | $NO_2$ | 231—232° |
| p-aminophenol | HCl | ca 15% | V | OH | hydrochloride ca. 250° decomp. |
| p-aminobenzoic acid | HCl or $H_2SO_4$ | 8% 4% | VI | } COOH | 198—200° |

In addition, it was observed that $N_1$-amidine-$N_2$-arylurea, when boiled with aniline, can readily yield the corresponding carbanilides and guanidine, as a result of the cleavage of the molecule.

Thus, when $N_1$-amidine-$N_2$-(p-nitrophenyl)-urea hydrochloride (III) was boiled with aniline, p-nitrocarbanilide (VII) and guanidine hydrochloride resulted;

The cleavage of the carboxy-derivative (VI) was accompanied by decarboxylation, and carbanilide (VIII) was formed.



The method can be used as a general way of forming $N_1$, $N_2$-disubstituted ureas, hitherto prepared usually from isocyanides and amines [7] [8], [9].

It seems possible that the carbanilides are produced through the intermediate formation of isocyanides:

$$Ar-NH-CO-NH-\underset{\underset{NH}{\|}}{C}-NH_2\cdot HCl \rightarrow Ar-N=C=O + \begin{bmatrix} C \diagdown_{NH_2}^{NH_2} \\ \diagdown NH_3 \end{bmatrix} HCl$$
$$\downarrow + NH_2C_6H_5$$
$$Ar-NH-CO-NHC_6H_5$$

As the reaction is very rapid, no intermediate product could be isolated.

The products (III)—(VI) have been tested with regard to their bacteriostatic action *in vitro* against *saprophytic Mycobacteria* by prof. S. Ślopek of the Silesian Medical Academy in Rokitnica.

The product (III) showed a relatively strong inhibiting action at concentrations of 5—15 mg per 100 ml. The products (IV) and (V) showed a weaker action and the derivative of p-aminobenzoic acid (VI) produced no inhibiting action at all.

We are much indebted to prof. Ślopek for carrying out these experiments.

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